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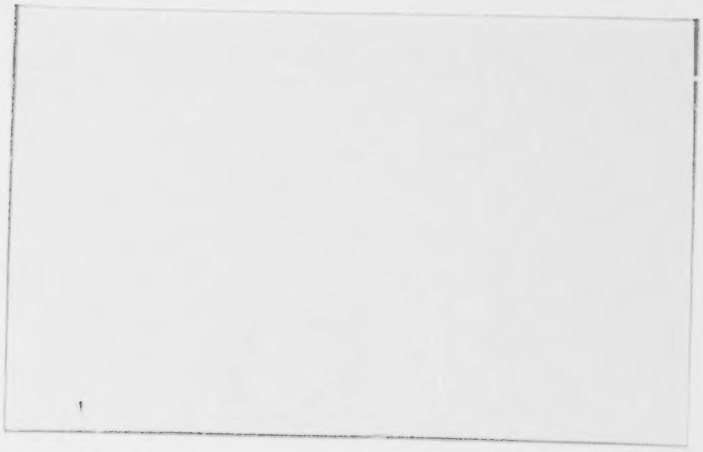

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FINAL REPORT
VOLUME II

APCO Contract No. CPA 70-45

A STUDY OF THE LIMESTONE INJECTION WET SCRUBBING PROCESS

Presented to:

AIR POLLUTION CONTROL OFFICE
DEPARTMENT OF HEALTH, EDUCATION AND WELFARE
411 West Chapel Hill Street
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1 November 1971

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16. Abstracts The volume contains three technical notes relating to the limestone injection wet scrubbing process. (1) Calculation of the Enthalpy of Aqueous Ionic Solutions. This technical note outlines the method for calculating enthalpy: The thermodynamic basis is given, the derivation of the equations for the difference between ideality and reference state are given, and the means of selecting the reference states are discussed. Finally a comparison is made between experimental and calculated values. (2) Description of the Radian Process Model for the Prototype LIWS System. This technical note presents a description of the Radian process model. A brief description of the LIWS process with regard to its relationship to the process model is followed by listing of the model assumptions and parameters. Included is a detailed description of the model. (3) Equilibrium Calculations for Type I APCO Inhouse Experiments. This technical note gives the results of equilibrium calculations made during analysis of data from SO_2 scrubbing experiments.

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TECHNICAL NOTE 200-004-12

CALCULATION OF THE ENTHALPY OF AQUEOUS IONIC SOLUTIONS

Prepared by:

David W. DeBerry
Philip S. Lowell

25 August 1970

1.0 INTRODUCTION

Key ingredients in chemical process design or analysis are the energy and material balances. This is true for the lime/limestone wet scrubbing process. This process involves gas, liquid, and solid stream components. The energy balance involves sensible heats, latent heats, heats of reaction, and heats of mixing.

This technical note is concerned with the aqueous solution. It takes into account the various ionic and non-ionic species present, their heats of reaction, and their heats of dilution. With the ability to calculate the enthalpy of the total liquid phase, data may be analyzed more accurately. Also the effect of the chemical reaction system in the liquid phase may be calculated. Without a computational scheme such as is presented here, not even the order of magnitude of the ionic reaction system and liquid phase non-ideality could be estimated.

A classical chemical engineering approach was used to solve this problem. The total enthalpy of the solution is the sum of the partial molal enthalpies of the solution components. The partial molal enthalpy of each solution component was calculated as the sum of the reference state enthalpy and the difference between the partial molal enthalpy and the reference state enthalpy.

In addition to this classical approach for enthalpy calculation, the enthalpy and equilibrium calculations made by Radian are put on a thermodynamically consistent basis. The standard state heat of reaction is related to the change of the equilibrium constant of that reaction with temperature. The

heats of dilution of the solution components are related to the change in the activity coefficients with temperature. These relationships between equilibrium data and enthalpy data are accounted for on a thermodynamically consistent basis.

The following method for calculating enthalpy is outlined in this technical note. First the thermodynamic basis is given. Second the derivation of the equations for the difference between ideality and reference state are given. Then the means of selecting the reference states are discussed. Finally a comparison is made between experimental and calculated values.

2.0 THEORY

The Gibbs free energy of an actual reaction is given in Equation 1.

$$\Delta G = \Delta H - T\Delta S \qquad (1)$$

The heat of the reaction is given by the Gibbs-Helmholtz equation, Equation 2.

$$\frac{-\Delta H}{T^2} = \frac{\partial(\Delta G/T)}{\partial T} \qquad (2)$$

The free energy may be considered to be composed of two parts, a standard state free energy plus a deviation from the standard state.

$$\Delta G = \Delta G^\circ + \Delta G^M \qquad (3)$$

Hence the enthalpy may be considered to be composed of two parts as in Equation 4.

$$\frac{-\Delta H}{T^2} = \frac{\partial(\Delta G^\circ/T)}{\partial T} + \frac{\partial(\Delta G^M/T)}{\partial T} \qquad (4a)$$

$$= \frac{-\Delta H^\circ}{T^2} + \frac{-\Delta H^M}{T^2} \qquad (4b)$$

The first term, the contribution in going from reactant reference state to produce reference state, is given in Equation 5 for a J+1 component system

$$\Delta H^\circ = \sum_{j=1}^{J+1} n_j H_j^\circ \qquad (5)$$

The various H_j° values need to be determined. As an example consider the ionization of water

$$H_2O \rightleftarrows H^+ + OH^- \qquad (6)$$

The free energy of this reaction from standard state to standard state is known as a function of temperature and hence the standard state heat of the reaction is known from Equation 4. The enthalpy of water is known and the enthalpy of the hydrogen ion at infinite dilution (reference state for H^+) is arbitrarily set equal to zero at 25°C. The enthalpy of the hydroxyl ion may be calculated as shown in Equation 7.

$$H^\circ_{OH^-} = H^\circ_{H_2O} - H^\circ_{H^+} + \Delta H^\circ_R \qquad (7)$$

This method may be used to calculate the reference state enthalpy of the various species in the solution. As may be seen, there may be several different paths from which the value of a reference state enthalpy may be calculated. An effort must be made to use that path that seems to have the most reliable data.

The second term in Equation 3 is the free energy associated with the difference between reference state and actual state conditions. For a J+1 component system the free energy of mixing is given by

$$\Delta G^M = RT \sum_{j=1}^{J+1} n_j \ell n a_j \tag{8}$$

Substituting Equation 8 into Equation 4 yields the expression for the heat of mixing.

$$-\Delta H^M = RT^2 \sum_{j=1}^{J+1} n_j \frac{\partial \ell n a_j}{\partial T} \tag{9}$$

The problem of calculating enthalpies is that of evaluating Equations 5 and 9 in the units that are appropriate to our problem.

The total enthalpy, H, of a system is related to the partial molal enthalpies of the J+1 constituents of the system by the following equation.

$$H = n_1 \overline{H}_1 + n_2 \overline{H}_2 + \ldots = \sum_{j=1}^{J+1} n_j \overline{H}_j \tag{10}$$

For aqueous solution it is convenient to use the molalities of the species instead of the number of moles. We define the molality of the $j^{\underline{th}}$ species in the following way.

$$m_j = \frac{n_j}{n_W M_W} = \frac{n_j m_W}{n_W} \tag{11}$$

M_W is the molecular weight of water with the units kg/mole. It is also convenient to express the partial molal enthalpy as the sum of the deviation from standard state, $\overline{H}_j - H_j^\circ$, plus its standard state value, H_j°.

$$\overline{H}_j = \left(\overline{H}_j - H_j^\circ\right) + H_j^\circ \tag{12}$$

With these definitions, the total enthalpy can be expressed as in Equation 13.

$$H = \frac{n_W}{m_W} \sum_{j=1}^{J+1} m_j\left[\left(\overline{H}_j - H_j^\circ\right) + H_j^\circ\right] \tag{13}$$

Separating the water term, we obtain Equation 14.

$$H = n_W\left\{\left(\overline{H}_W - H_W^\circ\right) + H^\circ{}_W + \frac{1}{m_W} \sum_{j=1}^{J} m_j\left[\left(\overline{H}_j - H_j^\circ\right) + H_j^\circ\right]\right\} \tag{14}$$

This is the general equation which we will use for the energy balance. The molalities of the species may be calculated using the Radian chemical equilibrium program. The calculation of the deviation terms and standard state enthalpies is discussed below.

The deviation from the standard state may be calculated from the variation of the activity coefficient with temperature.

$$\left(\bar{H}_j - H_j^\circ\right) = -RT^2 \frac{\partial \ell n a_j}{\partial T} = -RT^2 \frac{\partial \ell n \gamma_j}{\partial T} \qquad (15)$$

We will derive two separate expressions, one for the species in solution, and one for water.

In the Radian model, the activity coefficients of the species in solution are given by the following equation.

$$\ell n \gamma_j = A z_j^2 \ell n 10 \left[\frac{-I^{\frac{1}{2}}}{1 + \mathring{a}_j B I^{\frac{1}{2}}} + b_j I\right] + U_j I \qquad (16)$$

For the present we must assume that only A and B are functions of temperature.

$$A = \frac{1.8246 \times 10^6}{(DT)^{3/2}} \, d_o^{\frac{1}{2}} \qquad (17a)$$

$$B = \frac{50.29 d_o^{\frac{1}{2}}}{(DT)^{\frac{1}{2}}} \qquad (17b)$$

These coefficients contain the temperature as well as the dielectric constant (D) and the density of water (d_o) which are functions of temperature. Differentiating $\ell n \gamma_i$ we obtain Equation 18.

$$\frac{\partial \ell n \gamma_i}{\partial T} = z_j^2 (\ell n 10) \left\{\frac{\partial A}{\partial T}\left[\frac{-I^{\frac{1}{2}}}{1 + \mathring{a}_j B I^{\frac{1}{2}}} + b_j I\right] + A \frac{\partial B}{\partial T}\left[\frac{\mathring{a}_i I}{(1+\mathring{a}_j B I^{\frac{1}{2}})^2}\right]\right\} \qquad (18)$$

In evaluating the derivatives of A and B we will use the following definitions.

$$\alpha \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = \frac{-1}{d_o}\left(\frac{\partial d_o}{\partial T}\right)_p \tag{19}$$

$$\tau \equiv \frac{1}{D}\frac{\partial D}{\partial T} + \frac{1}{T} \tag{20}$$

Differentiating A and B and using these definitions we obtain Equations 21 and 22.

$$\frac{\partial A}{\partial T} = -\frac{3}{2} A \left(\tau + \frac{\alpha}{3}\right) \tag{21}$$

$$\frac{\partial B}{\partial T} = -\frac{1}{2} B \left(\tau + \alpha\right) \tag{22}$$

Combining Equations 15, 18, 21, and 22, and using the definition $\beta_j = \mathring{a}_j B I^{\frac{1}{2}}$, yields the desired expression for the relative partial molal enthalpy of the $j^{\underline{th}}$ species in solution.

$$\left(\overline{H}_j - H_j^\circ\right) = \frac{RT^2 A z_j^2 \ell n 10}{2}\left\{3\left(\tau + \frac{\alpha}{3}\right) b_j I - \frac{I^{\frac{1}{2}}\left[2\beta_j \tau + 3\left(\tau + \frac{\alpha}{3}\right)\right]}{\left(1 + B_j\right)^2}\right\} \tag{23}$$

The expression for the relative partial molal enthalpy of water is analogous to that given for the solution species.

$$\left(\overline{H}_w - H_w^\circ\right) = -RT^2 \frac{\partial \ell n \gamma_w}{\partial T} = -RT^2 \frac{\partial \ell n a_w}{\partial T} \tag{24}$$

The derivation of an expression for $\ell n a_w$ was given in Radian Technical Note 200-004-02, 27 May 1970. The result is shown in Equation 25.

$$-\ell n a_w = \frac{\ell n 10}{m_w} \sum_{j=1}^{J} m_j \left\{ \frac{-A z_j^2 I^{\frac{1}{2}}}{\beta_j^3} \left[\beta_j - 2\ell n\left(1 + \beta_j\right) + \frac{\beta_j}{1 + \beta_j} \right] \right.$$

$$\left. + \frac{I}{2} \left[A z_j^2 b_j + U_j \right] \right\} + \frac{1}{m_w} \sum_j m_j \qquad (25)$$

Once again we assume that only A and B are functions of temperature

$$\frac{\partial \ell n a_w}{\partial T} = \frac{\partial A}{\partial T} \frac{\partial \ell n a_w}{\partial A} + \frac{\partial B}{\partial T} \sum_{j=1}^{J} \frac{\partial \beta_j}{\partial B} \frac{\partial \ell n a_w}{\partial \beta_j} \qquad (26)$$

After performing the differentiations of $\ell n a_w$, we can use our previous results to obtain $(\bar{H}_w - H_w^\circ)$.

$$(\bar{H}_w - H_w^\circ) = \frac{RT^2}{2} \left\{ 3\left(\tau + \frac{\alpha}{3}\right) \left[\ell n a_w + \frac{\ell n 10}{m_w} \sum_{j=1}^{J} m_j \left(\frac{U_j I}{2} + \frac{1}{\ell n 10} \right) \right] \right.$$

$$- A(\tau + \alpha) \frac{I^{\frac{1}{2}} \ell n 10}{m_w} \sum_{j=1}^{J} \frac{m_j z_j^2}{\beta_j^2} \left[-\frac{6}{\beta_j} \ell n\left(1 + \beta_j\right) \right.$$

$$\left. \left. + \frac{6 + 9\beta_j + 2\beta_j^2}{\left(1 + \beta_j\right)^2} \right] \right\} \qquad (27)$$

The remaining quantities necessary for the enthalpy calculation are the standard state enthalpies, H_j°. The standard state heats of formation were chosen for this application. This

enables us to select a certain number of "key" enthalpy values and then calculate the rest from heats of reaction.

The selected standard state heats of formation of the key species are given in Table I. The values for the aqueous species are based on the assignment of $H_f^\circ = 0$ for $H^+(aq)$ at 25°C. The values given are those which are considered to be the most accurate and which should give the best relative accuracy in the computational chain.

The standard state heat of reaction may be calculated from the variation of the equilibrium constant with respect to temperature.

$$\frac{\partial \ell nK}{\partial T} = \frac{\Delta H_R^\circ}{RT^2} \qquad (28)$$

The data for ℓnK as a function of temperature used in the Radian chemical equilibrium program were used to calculate ΔH_R° at 25°C for each reaction. Using these heats of reaction and the selected heats of formation, the remaining heats of formation at 25°C were calculated by the following equation.

$$\Delta H_R^\circ = \sum_j e_{p_j} H_{f_j}^\circ (\text{product}) - \sum_j e_{r_j} H_{f_j}^\circ (\text{reactant}) \qquad (29)$$

These values are given in Table II.

Heat capacities are necessary for calculating the heats of formation at temperatures other than 25°C. The literature survey and preliminary calculations indicated that the mean heat capacities calculated by Criss and Cobble (CO-001) from their entropy correspondence principle would give

TABLE I

HEATS OF FORMATION OF THE KEY SPECIES AT 25°C

Species	$H^{\circ}_{f,298.16}$ (kcal/mole)
$H_2O(\ell)$	- 68.317
$H^+(aq)$	0.00
$SO_4^=(aq)$	-216.90
$NO_3^-(aq)$	- 49.372
$Ca^{++}(aq)$	-129.77
$SO_2(g)$	- 70.93
$CO_2(g)$	- 94.01
$Cl^-(aq)$	- 40.023
$Mg^{++}(aq)$	-110.41
$Na^+(aq)$	- 57.279

TABLE II

STANDARD STATE HEATS OF FORMATION AND MEAN HEAT CAPACITIES OF LIQUID SPECIES

Species	$H^\circ_{f,298.16}\left(\frac{kcal}{mole}\right)$	$C^\circ_p\Big]_{25}^{60^\circ C}\left(\frac{cal}{mole^\circ K}\right)$
H_2O	- 68.317	18.04
H^+	0.000	23.
OH^-	- 54.799	- 47.
HSO_3^-	-149.376	- 16.
$SO_3^=$	-152.276	-121.
$SO_4^=$	-216.900	- 99.
HCO_3^-	-164.729	- 27.
$CO_3^=$	-162.126	-132.
NO_3^-	- 49.372	- 49.
HSO_4^-	-211.660	- 13.
H_2SO_3	-145.516	+ 7.
H_2CO_3	-166.971	91.
Ca^{++}	-129.770	45.
$CaOH^+$	-183.320	- 2.
$CaSO_3^\circ$	-279.736	- 76.
$CaCO_3^\circ$	-289.720	- 87.
$CaHCO_3^+$	-293.118	18.
$CaSO_4^\circ$	-344.033	- 8.
$CaNO_3^+$	-173.445	- 4.
Mg^{++}	-110.410	51.
$MgOH^+$	-162.839	4.

continued

TABLE II (continued)

Species	$H^\circ_{f,298.16}\left(\frac{kcal}{mole}\right)$	$C^\circ_p]^{25^\circ C}_{as}\left(\frac{cal}{mole^\circ K}\right)$
$MgSO_3^\circ$	-260.707	- 70.
$MgHCO_3^+$	-274.063	24.
$MgSO_4^\circ$	-322.469	- 48.
$MgCO_3^\circ$	-270.226	- 81.
Na^+	- 57.279	35.
$NaOH^\circ$	-112.078	- 12.
$NaCO_3^-$	-218.017	- 97.
$NaHCO_3^\circ$	-222.008	8.
$NaSO_4^-$	-273.076	- 64.
$NaNO_3^\circ$	-106.651	- 14.
Cl^-	- 40.023	- 51.

satisfactory results. Using this form, the heats of formation at a temperature between 25 and 60°C are given by Equation 30.

$$H^{\circ}_{f_j}(T) = H^{\circ}_{f_j}(298.16) + C_{p,j}\Big]_{25}^{60} (T - 298.16) \qquad (30)$$

All of the pertinent values given by CO-001 were adopted. Missing values were calculated from the ΔC_p of reaction and a computational scheme similar to the one given for the enthalpies. This procedure is subject to greater inaccuracies, however, since the calculation of ΔC_p requires a second differentiation of $\ln K$. Most of the equilibria data do not justify this operation. The calculated and adopted values for $C_{p,j}\Big]_{25}^{60}$ are also given in Table II.

The equations and data necessary for the enthalpy calculation were incorporated into a computer subroutine. Functional forms for some of the coefficients such as α and d_o were obtained by curve fitting tabular data. The comparison of experimental and calculated results is given in the next section.

3.0 COMPARISON OF EXPERIMENTAL AND CALCULATED RESULTS

Thermodynamic values were calculated for several simple systems and compared with experimental values. The integral heats of solution at a given molality was used for most of the comparisons. In terms of the calculated total enthalpy, H, the integral heat of solution of a single salt in water at a given temperature is given by:

$$\Delta H_{soln.} = 1/n_s[H - n_w H^{\circ}_w - n_s H^{\circ}_s] \qquad (31)$$

H_w° and H_s° are the heats of formation of water and pure solute respectively, and n_w and n_s are the corresponding number of moles of water and solute. This equation was used to calculate $\Delta H_{soln.}$ for HCl(g), $CaCl_2$(s), and $Ca(OH)_2$(s).

The relative partial molal enthalpy of the total solute, $\overline{L}_2$, was also calculated for several cases. This is essentially the "deviation" term given by

$$\overline{L}_2 = \sum_{j=1}^{J} v_j \left(\overline{H}_j - H_j^\circ\right) \qquad (32a)$$

$$\overline{L}_1 = \left(\overline{H}_w - H_w^\circ\right) \qquad (32b)$$

where v_j is the number of anions or cations which one electrolyte molecule dissociates into. The results of these calculations are given in Table III. In general the agreement is good. The present model does not predict the maximum in $\overline{L}_2$ shown by NaCl.

TABLE III

COMPARISON OF EXPERIMENTAL AND CALCULATED RESULTS @ 25°C

Solute	Molality (mole/kg H_2O)	Experimental ΔH_{soln} (cal/mole)	Calculated ΔH_{soln} (cal/mole)	Experimental $\bar{L}_2$ (cal/mole)	Calculated $\bar{L}_2$ (cal/mole)
HCL(g)	0.04	-17,800	-17,895		
$CaCl_2$(s)	0.02	-19,560	-19,560	360	339
	0.05	-------	-------	490	443
	0.10	-------	-------	620	517
	0.60	-------	-------	1020	529
$Ca(OH)_2$(s)	0.004	- 4,082	- 3,525		
	0.01	- 3,819	- 3,400		
	0.02	- 3,523	- 3,345		
NaCl	0.06	-------	-------	94	112
	0.37	-------	-------	42	181

4.0 NOMENCLATURE

a	activity
$\mathring{a}$	ion size activity coefficient parameter
A	Debye-Hückel limiting slope constant
b	activity coefficient deviation parameter
B	Debye-Hückel constant
C_p	heat capacity
d_o	density of water
D	dielectric constant of water
G	Gibbs free energy
H	enthalpy, total
$\overline{H}$	partial molal enthalpy
$H°$	reference state enthalpy
H^M	heat of mixing
I	ionic strength
J	number of species except for water
K	equilibrium constant
$\overline{L}$	relative partial molal enthalpy
m	molality

M	molecular weight
n	mole
R	gas constant
S	entropy
T	absolute temperature
U	activity coefficient parameter
v	number of ions formed from one mole of solute
V	volume
z	ion charge

Greek

α	derivative term defined by eq 19
β	the term $\mathring{a}BI^{\frac{1}{2}}$
γ	activity coefficient
τ	derivative term defined by eq 20

Subscripts

j	$j^{\underline{th}}$ species
s	solute
w	water

5.0 BIBLIOGRAPHY

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TECHNICAL NOTE 200-004-19

DESCRIPTION OF THE RADIAN PROCESS MODEL FOR THE PROTOTYPE LIWS SYSTEM

22 March 1971

Prepared by:

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CHEMICAL RESEARCH • SYSTEMS ANALYSIS • COMPUTER SCIENCE • CHEMICAL ENGINEERING

I. INTRODUCTION

Radian has developed a computerized process model for the limestone injection - wet scrubbing (LIWS) process. The process model is based upon (1) the ability to predict vapor-liquid-solid equilibria for the CaO-MgO-Na_2O-SO_2-CO_2-SO_3-N_2O_5-HCl-H_2O system and (2) a number of process assumptions with regard to equipment characterization and the extent of various chemical reactions.

Much of the theoretical basis for this process model was developed under APCO Contract No. CPA 22-69-138 and is described in the Radian Final Report "A Theoretical Description of the Limestone Injection - Wet Scrubbing Process". The computerized process model used (1) employs a modular approach to performing process material and energy balances, (2) specifies the extent of various reaction steps by appropriate equilibrium assumptions or model inputs, (3) characterizes the various process vessels in terms of practical equipment descriptions, and (4) converges the model's iterative parameters with suitable numerical techniques.

This technical note presents a description of the Radian process model. A brief description of the LIWS process with regard to its relationship to the process model will be followed by listing of the model assumptions and parameters. After these discussions, a detailed description of the model will be presented.

The utility of this model to process development and design is clear. Simulation results for the prototype LIWS process are discussed in Radian Technical Note 200-004-18.

II. PROCESS DESCRIPTION

A qualitative description of how the Radian model relates to process operation will be presented in this section. The model description will be given in terms of the wet scrubbing scheme which represents the essential features of the prototype LIWS system being planned for TVA's Shawnee Plant at Paducah, Kentucky. The process description for other process schemes should follow by analogy to this one.

Figure II-1 is a schematic diagram showing the various process vessels and streams.

The scrubber serves as a gas-liquid contacting device with some dissolution of limestone solids. In the present model, the scrubber (S) is assumed to trap all of the solids in the flue gas stream so that no solids leave with the stack gas. For material balance calculations the inlet gas stream to the scrubber has been divided into two fractions, a flue gas stream (FG) containing only gaseous components and a limestone-fly ash stream (LA) containing only solid components. The solids are composed of two parts: limestone (LS) and flyash (FA). In this model the stack gas (SG) leaving the scrubber is assumed to be in equilibrium with the scrubber liquor (and thus with the scrubber bottoms).

The scrubber effluent hold tank (E) serves mainly as a solids dissolution and precipitation vessel. This stirred tank should approximate idealized backmix flow and in practice should be designed to provide enough residence time and agitation to hydrate and dissolve the major portion of the CaO and MgO that dissolves in the system. In this model some CaO and MgO entering the stream are taken to be unreactive. This amount of CaO and MgO leaves the system unreacted in the filter

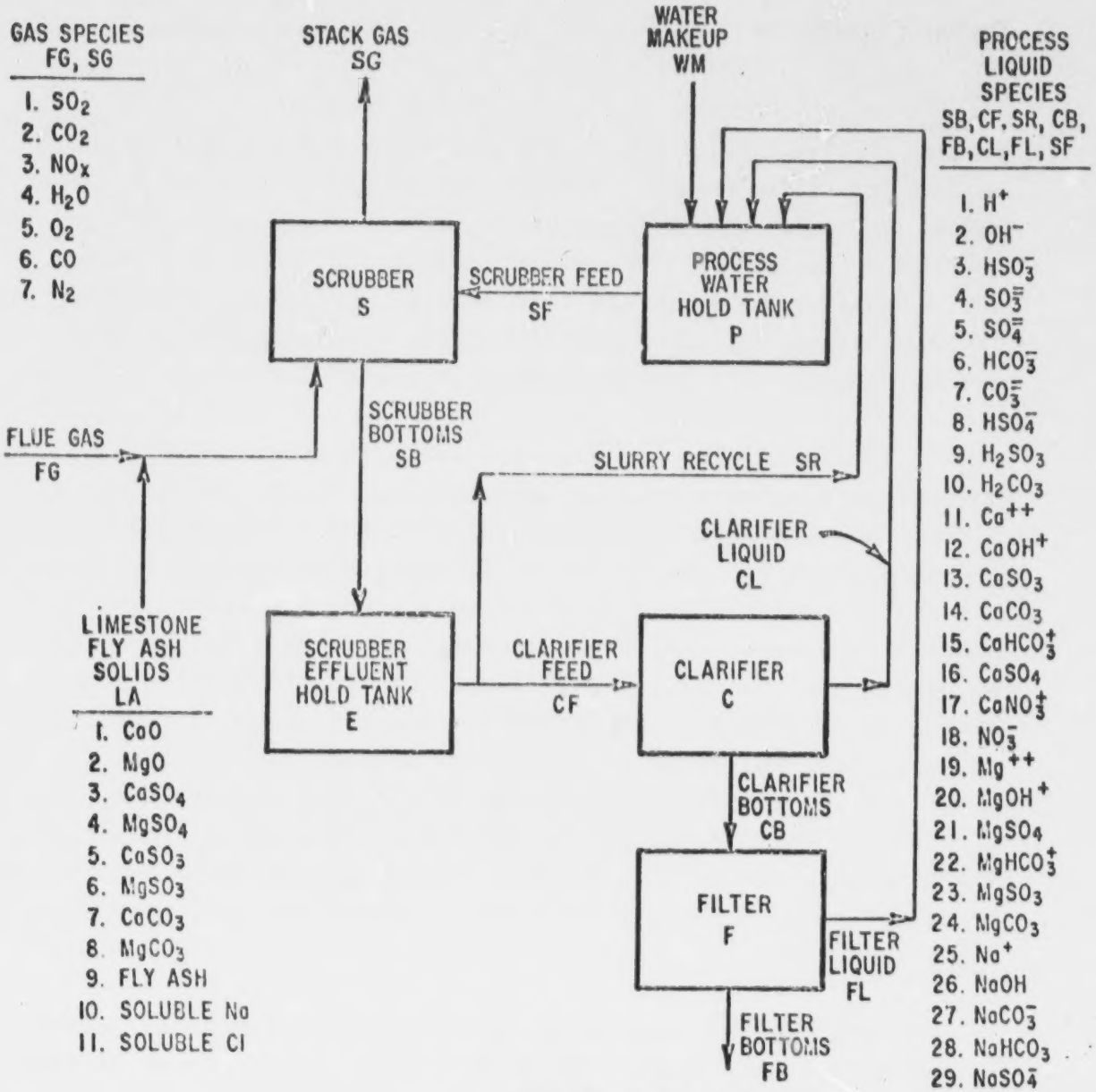

FIGURE II-1 WET SCRUBBING SCHEME

25 Radian

bottoms (FB) stream. All of the remaining CaO and MgO which enters the effluent hold tank (E) is assumed to be available for reactions. The liquid leaving the effluent hold tank (E) is assumed to be in equilibrium with respect to the liquid and solid phases. This implies that several species will dissolve or precipitate. A major portion of the precipitation in an actual process will probably occur in the effluent hold tank.

The clarifier and filter vessels serve mainly as solid-liquid separators. In the model presented, the clarifier liquid (CL) was assumed to be in equilibrium with the solids in the clarifier. The liquid in the clarifier bottoms (CB) was assumed to have the same composition as the CL stream. This model also assumes that the compositions of the solid and liquid phases in streams leaving the filter (FB and FL) are the same as the compositions of the solid and liquid in equilibrium in the clarifier and filter. This situation would exist if the clarifier and filter were operated at the same temperature, or if the solid-liquid "shift" in the filter were insignificant. The CL and FL streams can contain a small amount of solids due to clarifier and filter inefficiencies which are specified as model inputs.

The process water hold tank (P) is a stirred tank which serves as a liquid mixer. Here the clarifier and filter liquids (CL and FL) and slurry recycle (SR) are diluted with water make-up (WM) to produce the scrubber feed (SF) for the scrubber. In this model, this tank is assumed to be an ideally backmixed vessel that has attained solid-liquid equilibrium.

Figure II-1 also shows the chemical species possibly present in various process streams. Seven gaseous species are listed for the flue and stack gases. The nitrogen oxides in

the gas phase are designated NO_x since not enough information concerning (1) NO_x composition in the gas phase, (2) oxidation rates, and (3) chemical reactions in liquid phase has been found in the literature. Due to this uncertainty, a realistic fraction of the NO_x in the flue gas will be taken as absorbing and this NO_x will show up in the process liquids as "equivalent nitrates". A refinement of this approximation can be made if enough information concerning the NO_x system becomes available.

The limestone - fly ash stream (LA) could contain eleven solid species, CaO and MgO being the major ones. The fly ash component is not specified in further detail because fly ash compositions vary to some extent and because the soluble nature of the fly ash is not fully known at this point. For the purposes of this model, the fly ash will be assumed to contain Na_2O, NaCl, and inerts.

III. MODEL ASSUMPTIONS AND PARAMETERS

The present Radian model is based upon the following assumptions:

(1) The partial pressures of SO_2, CO_2, and H_2O in the stack gas leaving the scrubber are in equilibrium with the scrubber liquid at the scrubber temperature.

(2) After withholding a portion of the input lime (CaO and MgO) as being chemically unreacted in the system, solid-liquid equilibrium is achieved in the scrubber-effluent hold tank and the process-water hold tank.

(3) The clarifier and filter are solid-liquid separators only (no chemical change occurs).

(4) Ionic reactions taking place in the liquid phase are rapid and thus at equilibrium.

The first assumption is based on the premise that the gas-liquid absorption step is not rate controlling, whereas the second assumes the hold tanks are large enough to permit solid-liquid equilibrium except for a portion of unreactive lime. This unreacted lime (CaO and MgO) is fixed by model input.

The compositions for the system inlet and exit streams [limestone (LS), fly ash (FA), flue gas (FG), stack gas (SG), and water makeup (WM)] and operating conditions for the process are model inputs. Other model parameters are used to set the "conversion" in the process due to various rate steps. That is to say, the fraction of precipitating solids, limestone in the flue gas entering the scrubber and dissolving, sulfite oxidizing, and NO_x absorbed in the scrubber are set by the model parameters.

A list of the model parameters along with their typical units is given below:

1. Theoretical Limestone $\left[\frac{\text{moles CaO + MgO in LS}}{\text{moles } SO_2 \text{ in FG}}\right]$

2. Lime Hydrating in System $\left[1 - \frac{\text{moles CaO + MgO in FB}}{\text{moles CaO + MgO in LS}}\right]$

3. Lime Hydrating in Scrubber $\left[\frac{\text{moles CaO+MgO from LS hydrating}}{\text{moles CaO+MgO in LS}}\right]$

4. Limestone Solids Dissolving
$\left[1 - \frac{\text{moles } Ca(OH)_2 + Mg(OH)_2 \text{ from LS left in SB}}{\text{moles } Ca(OH)_2 + Mg(OH)_2 \text{ from LS}}\right]$

5. Recycled Solids Dissolving

$$\left[1 - \frac{Ca(OH)_2 + Mg(OH)_2 \text{ from SF left in SB}}{\text{moles } Ca(OH)_2 + Mg(OH)_2 \text{ from SF}}\right]$$

6. Limestone Composition $\left[\frac{\text{moles MgO in LS}}{\text{moles CaO + MgO in LS}}\right]$

7. Fly Ash Level $\left[\frac{\text{wt. fly ash}}{\text{wt. sulfur in coal}}\right]$

8. Soluble Sodium [wt. fr. Na in FA]

9. Soluble Chlorine [wt. fr. Cl in FA]

10. SO_2 Level in Flue Gas [mole fr. SO_2]

11. SO_2 Absorbed $\left[\frac{\text{moles } SO_2 \text{ absorbed}}{\text{mole } SO_2 \text{ in FG}}\right]$

12. Sulfite Oxidized $\left[\frac{\text{moles } SO_2 \text{ oxidized}}{\text{mole } SO_2 \text{ absorbed}}\right]$

13. CO_2 Level in Flue Gas [mole fr. CO_2]

14. NO Level in Flue Gas [mole fr. NO]

    NO_2 Level in Flue Gas [mole fr. NO_2]

15. NO Absorbed $\left[\frac{\text{moles NO absorbed}}{\text{moles NO in FG}}\right]$

    NO_2 Absorbed $\left[\frac{\text{moles } NO_2 \text{ absorbed}}{\text{moles } NO_2 \text{ in FG}}\right]$

16. Solids in Filter Bottoms [wt. fr. solids in FB]

17. Solids in Clarifier Bottoms [wt. fr. solids in CB]

18. Filter Efficiency $\left[\frac{\text{wt. solids in FB}}{\text{wt. solids in filter inlet}}\right]$

19. Clarifier Efficiency $\left[\frac{\text{wt. solids in CB}}{\text{wt. solids in clarifier inlet}}\right]$

20. Solids Precipitated in Scrubber [yes or no]

21. Circulating Liquor Temperature [°F]

22. Scrubber Feed Rate $\left[\frac{\text{Gal. of SF}}{\text{1000 ACF of FG}}\right]$

Actually, the temperature of the scrubber liquor is determined by an energy balance about the scrubber. (Here, the humidity and temperature of the flue gas are the dominant factors.) Then the tempterature of the circulating liquor is set equal to that of the scrubber liquor.

Process simulations have been conducted by specifying the amount of SO_2 to be removed from a flue gas of known composition and adjusting the amount of slurry recycle (SR) (or the amount of scrubber feed (SF) in some cases) to obtain this SO_2 removal. In these cases, the fractions of limestone solids (LS) reacting in the scrubber have been specified as a model input. In the same way, the fractions of solid species in the scrubber feed (SF) stream that are available for reaction are also model inputs.

All of the liquid-phase species are allowed to react in the scrubber. Thus, for a fixed scrubber feed (SF) rate, the amount of slurry recycle (SR) required to obtain the desired SO_2 removal is a measure of the scrubbing capability of the process. High slurry recycle rates indicate a poor set of scrubbing parameters.

IV. COMPUTERIZED PROCESS MODEL

The computerized process model consists of essentially three parts: (1) an executive system that interconnects the processing units in appropriate fashion and controls the sequencing of computer operations, (2) equipment subroutines that model each process unit, and (3) convergence subroutines that force convergence of the model's iterative parameters.

The design of any one of these parts is dependent upon the design of the other parts. For example, a generalized scheme for performing material and energy balance calculations is attractive from the standpoint of model flexibility. However, this approach suffers from the need of greater programming sophistication and from less specific (and thus slower) convergency routines.

Radian has developed a computerized model that is based upon a compromise between generalization for greater system flexibility and specialization for improved computational efficiency. The modular concept for equipment subroutines has been used. This concept tends to allow greater flexibility in simulating various processing schemes. These equipment subroutines are specialized only to the extent that more rapid convergency can be obtained by using the engineer's knowledge of the system. Wherever possible the equipment subroutines were formulated to allow for extension to models which give a more sophisticated description of the processing unit.

A. Executive System

The function of the executive system is to interconnect the various process units in the appropriate fashion and control the sequencing of the computer operations.

The process units are interconnected by means of a "process matrix" during an initialization phase of computer operations. In this phase, model input data are read into the machine, the process matrix is used to define the processing scheme, and each equipment box is initialized. The interconnection of equipment boxes for the prototype system is shown in Figure IV-1. Here each processing unit is labeled by a number, its name, and the subroutine designation. For example, the subroutine used for the scrubber [equipment number (4)] is designated SCRUBR. In addition, the various process streams are labeled by letter abbreviation and a stream number.

The "process matrix" used to define this processing scheme is given on the first page of computer print-out for each simulation case. An example simulation case (Prototype Simulation No. 2-B) is given in the Appendix. The "process description" information defines the interconnection of process units. For example, equipment number 4 is the scrubber (subroutine SCRUBR). It has input streams numbered 2 and 15 and output streams numbered 3 and 6.

The executive system also must be given the order in which the process calculations are to be made. For the prototype simulations, the order of the process calculations was fixed. This order is indicated in the lower half of the first page of computer print-out. The order was selected so as to maximize computational efficiency. A block diagram showing the order of process calculations is given in Figure IV-2.

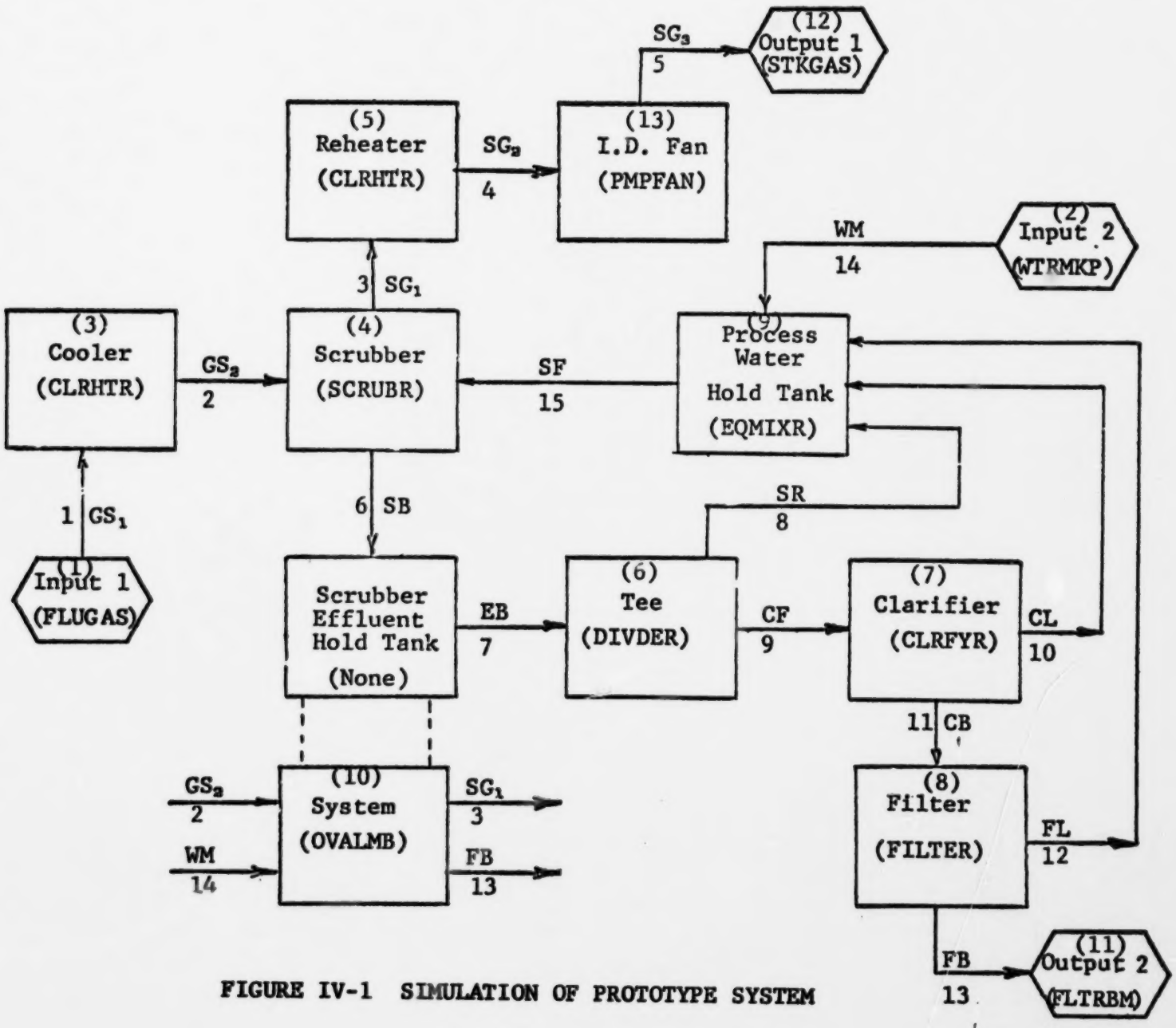

FIGURE IV-1 SIMULATION OF PROTOTYPE SYSTEM

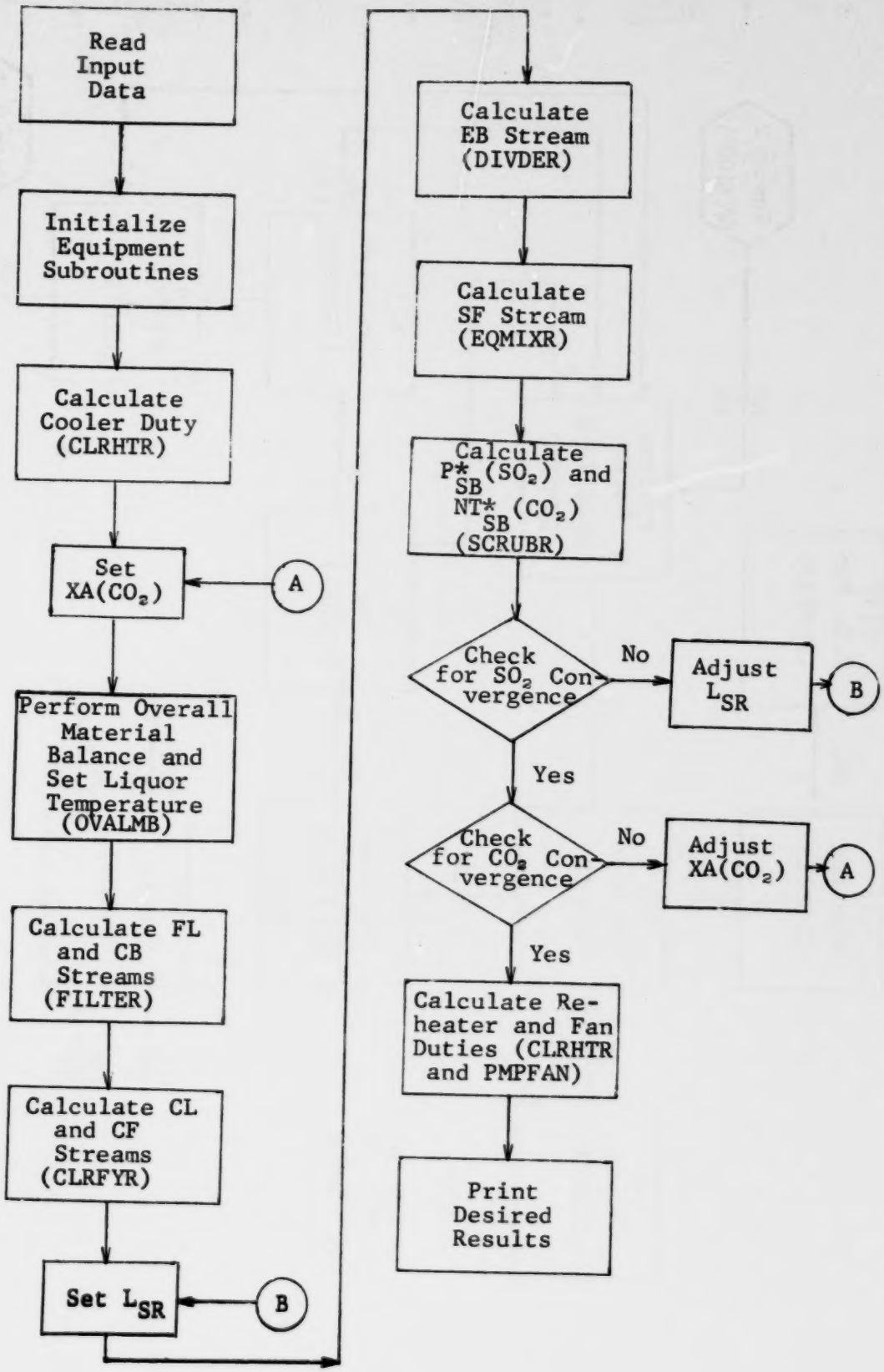

FIGURE IV-2 PROCESS CALCULATIONS FOR PROTOTYPE SIMULATIONS

After the initialization phase has been completed, the executive routine transfers control of computer operations to the appropriate subroutines until the process calculations have been converged. At this point, the calculated results are printed. The last ten pages of computer print-out (refer to attached case) show these results in the form of stream vector information. Stream vectors are the means by which information is transferred from one equipment routine to another.

B. Equipment Subroutines

Simulation of the prototype system involved the use of nine equipment subroutines.

1) Cooler (CLRHTR) - determines the heat exchange required to cool the flue gas stream to a specified scrubber inlet temperature.

2) Scrubber (SCRUBR) - determines if the scrubber feed stream contains enough basic species to scrub the specified amount of SO_2 from the flue gas and forces iteration until convergence is obtained.

3) Reheater (CLRHTR) - determines the heat exchange required to reheat the stack gas stream to a specified outlet temperature.

4) I.D. Fan (PMPFAN) - determines the energy required to pass the stack gas out of the system based upon pressure losses in the cooler, scrubber, and reheater.

5) Process Water Hold Tank (EQMIXR) - combines the process streams returning to the scrubber (slurry recycle, clarifier liquid, and filter liquid) with the water makeup and allows the exiting scrubber feed stream to reach solid-liquid equilibrium.

6) Filter (FILTER) - provides for solid-liquid separation based upon specified weight fraction solids in the filter bottoms stream.

7) Clarifier (CLRFYR) - provides for solid-liquid separation based upon specified amount of slurry recycle.

8) Tee (DIVDER) - divides the exit stream from the effluent hold tank into the slurry recycle and clarifier feed streams.

9) System (OVALMB) - determines the amount of water vaporized in the scrubber and the scrubber temperature using an approximate scrubber energy balance and then determines amount and composition of the filter bottoms stream using a system material balance.

Actually, the ninth process unit is the effluent hold tank. However, the System calculation routine eliminates the need

for effluent hold tank calculation. The same subroutine (CLRHTR) can be used for the cooler and the reheater.

In addition to these equipment subroutines, four "source" or "sink" type routines were required. Subroutines for the gas-solid stream (FLUGAS) and for the water makeup stream (WTRMKP) are used to "generate" the process input stream. Likewise, the exit stack gas (STKGAS) and filter bottoms (FLTRBM) stream are "discharged" as process exit streams. These last four subroutines essentially convert units for input/output purposes and provide a source or sink for the terminal process streams.

Each of the individual equipment subroutines will now be discussed in detail.

1. CLRHTR

This subroutine is used to calculate the heat required to cool or heat a process stream composed of a gas-solid stream from one temperature T_1 to another temperature T_2. In the prototype simulations, the CLRHTR subroutine is used for the cooler and reheater process units. Flow diagrams indicating the usage of CLRHTR for these units are given below.

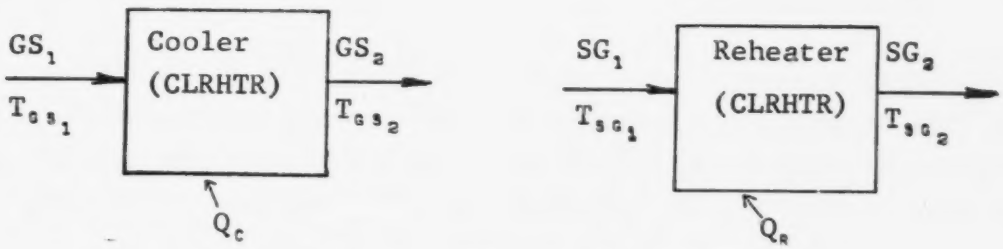

FIGURE IV-3. CLRHTR Flow Diagram

The subroutine inputs include (1) the temperature of the inlet gas-solid stream (T_1), the pressure of the inlet gas-solid stream (P_1), the number of moles of each gas and/or solid species in the inlet stream [$N_1(JG)$ and/or $N_1(JS)$], the temperature of the exit gas-solid stream (T_2), and the pressure drop across the heat exchanger ($-\Delta P_{HE}$). The basic assumption here is that all materials (both solid and gas) are at the same temperature.

The heat added to the process (Q) is then calculated by the relation:

$$Q = \Delta H_2 - \Delta H_1 \qquad \text{(IV-1)}$$

where 2 and 1 designate the outlet and inlet heat exchanger streams. By convention, Q is positive for heat added to the process. The enthalpies of process streams is calculated relative to a reference temperature of 25°C by means of an enthalpy subroutine.

The pressure of the outlet stream (P_2) is calculated by the relation:

$$P_2 = P_1 - (-\Delta P_{HE}) \qquad \text{(IV-2)}$$

2. SCRUBR

This subroutine is used to determine if the scrubber feed (SF) stream as calculated by means of other equipment routines throughout the system will indeed remove the specified fractions of SO_2 and CO_2 removal. In this version of SCRUBR,

the scrubbing liquor temperature is fixed by adiabatic humidification of the flue gas stream. This calculation is made in the OVALMB subroutine.

The input and output streams for the SCRUBR subroutine are shown below.

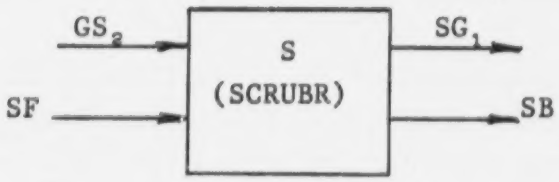

FIGURE IV-4. SCRUBR Flow Diagram

With the absence of rate correlations, the fractional conversions for the various rate steps occurring within the scrubber are specified by model assumptions or inputs. At the present time, sulfite oxidation and solid-liquid mass transfer rates are believed to be the rate controlling steps. Based upon this premise, the following assumptions have been made in this SCRUBR routine.

(1) The partial pressures of SO_2, CO_2, and H_2O in the stack gas leaving the scrubber are in equilibrium with the scrubber exit liquor (SB) at the scrubber temperature.

(2) All of the solids in the scrubber inlet gas-solid (GS_2) stream are trapped in the scrubber liquor.

(3) The fractions of CaO and MgO in the GS_2 stream that hydrate in the scrubber are fixed by model inputs.

(4) The fractions of solid species in the GS_2 or of the hydroxides formed from that stream that dissolve in the scrubber are fixed by model inputs.

(5) The fractions of solid species in the scrubber feed (SF) stream that dissolve in the scrubber are fixed by model inputs.

(6) The fraction of SO_2 entering the liquid from the gas that is oxidized in the scrubber is fixed by a model input. The circulating SO_2 is not oxidized.

(7) Solids precipitation can be allowed so that solid-liquid equilibrium is achieved with regard to the "reactive" chemical species or no precipitation is allowed.

The first assumption is one of vapor-liquid equilibrium. This describes scrubbers operated with the liquid-phase ideally backmixed so that the exit gas is last in contact with a liquor whose composition is the same as the scrubber bottoms (SB) stream. Examples are the turbulent contact absorber or marble-bed scrubber. For concurrent contactors (such as the venturi scrubber), the backmixed assumption is not necessary. It does not describe true countercurrent scrubbers.

The SCRUBR subroutine consists of essentially three parts. First, the total moles of "reactive" key species in the scrubber bottoms (SB) stream are determined as the sum of the "reactive" species entering the scrubber via the flue gas (FG), limestone-flyash (LA) stream, and the scrubber feed (SF) stream. For the nine key species (SO_2, CO_2, SO_3, N_2O_5, CaO, MgO, Na_2O, HCl, H_2O),

$$NT_{SB}(JT) = \Delta N_{SF,T}(JT) + \Delta N_{SD,T}(JT) + \Delta N_{A,T}(JT) \qquad \text{(IV-3)}$$

where $NT_{SB}(JT)$ are the total moles of key-species JT that should be considered in the equilibrium calculation of the SB stream, $\Delta N_{SF,T}(JT)$ are the moles of key-species JT that are available from the SF stream, $\Delta N_{SD,T}(JT)$ are the moles of key-species JT that are available from the LA stream due to dissolution, and $\Delta N_{A,T}(JT)$ are the moles of key-species that result from absorption from the FG stream. In these calculations, the species not available for reaction are withheld from the equilibrium calculation. For example, a fraction of the calcium hydroxide in the SF stream is specified by model input as reacting in the scrubber. The remaining fraction of calcium hydroxide is "withheld" from the scrubber equilibrium calculation.

The second phase of the SCRUBR routine involves "calling" the Radian chemical equilibrium program. This program calculates the equilibrium partial pressure of SO_2[$P^*_{SB}(SO_2)$] and the moles of total CO_2 in the SB liquid [$NT^*_{SB}(CO_2)$]. Here the desired partial pressure of CO_2 in the stack gas [$PP(CO_2)$] is specified as an equilibrium program input. The total moles of CO_2 in solution and compared with the total CO_2 determined by summing over the SF, FG, and LA streams [$NT_{SB}(CO_2)$].

Tests for SO_2 and CO_2 convergence are made using the following criteria:

$$\left| \frac{PP(SO_2) - P^*_{SB}(SO_2)}{PP(SO_2)} \right| < \varepsilon_{SO_2} \qquad \text{(IV-4)}$$

$$\left| \frac{NT_{SB}(CO_2) - NT^*_{SB}(CO_2)}{NT_{LA}(CaO) + NT_{LA}(MgO)} \right| < \varepsilon_{CO_2} \qquad \text{(IV-5)}$$

where $PP(SO_2)$ is the partial pressure of SO_2 in the stack gas and $NT_{LA}(CaO)$ and $NT_{LA}(MgO)$ are the moles of total CaO and total MgO entering the scrubber in the LA stream. If SO_2 and CO_2 convergence has not been attained for a given scrubber calculation, control is transferred to a convergence promotion subroutine whereby new values for the iterative parameters (scrubber feed rate or slurry recycle rate for the partial pressure of SO_2 and the fraction of CO_2 absorbed for the moles of CO_2 in SB) are selected.

The third and last phase of the SCRUBR subroutine involves adjusting the elements in the SB stream vector for quantities withheld in the scrubber equilibrium calculation.

In the present version of SCRUBR, the pressure drop across the scrubber ($-\Delta P_s$) is specified as an equipment parameter. The pressure of the scrubber exit gas (P_{s_1}) is calculated by

$$P_{s_1} = P_{s_2} - (-\Delta P_s) \qquad \text{(IV-6)}$$

3. PMPFAN

This subroutine calculates the power requirement of the I.D. fan. The pressure of the stack gas entering the fan is determined by the pressure losses through the cooler, scrubber, and reheater. The desired pressure of the exit stack gas stream is set by model input.

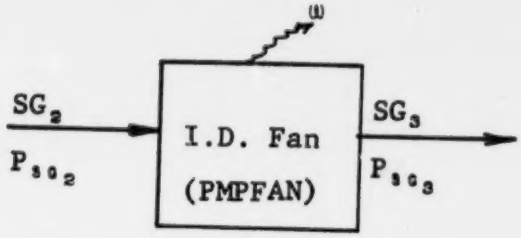

FIGURE IV-5

PMPFAN Flow Diagram

The power requirement ($-\omega$) is then calculated by the relation:

$$-\omega = C_f Q \cdot \left(P_{SG_3} - P_{SG_2}\right)/\eta_f \qquad \text{(IV-7)}$$

where C_f is the appropriate units conversion factor, Q is the gas flow rate, P_{SG_3} and P_{SG_2} are the exit and inlet gas pressures, and η_f is the efficiency of the fan.

4. EQMIXR

This subroutine sums the total moles of key species for all input streams and uses the equilibrium program to calculate the composition of the vessel's output stream. Here, the input streams are taken to be "known" streams and the output stream is calculated.

Thus, for the process water hold tank in the prototype simulations, the moles of key species in the slurry recycle (SR), clarifier liquid (CL), filter liquid (FL), and water

makeup (WM) streams are summed to give the key-species amounts in the scrubber feed (SF) stream, i.e.,

$$NT_{SF}(JT) = NT_{SR}(JT) + NT_{CL}(JT) + NT_{FL}(JT) + NT_{WM}(JT) \quad \text{(IV-8)}$$

where JT is the index for total or key species. Again, the nine key species are SO_2, CO_2, SO_3, N_2O_5, CaO, MgO, Na_2O, HCl and H_2O.

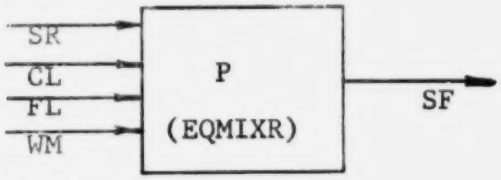

FIGURE IV-6

EQMIXR Flow Diagram

The process water hold tank is taken to be a well-stirred vessel which closely approaches solid-liquid equilibrium. Thus, the composition of the SF stream is computed as the equilibrium composition corresponding to the key-species amounts given by Equation (IV-8).

In this version of EQMIXR, the temperature of the vessel is set equal to the temperature of the filter liquid (FL) stream. This assumes that the circulating liquor system operates isothermally.

In addition to summing over the key species, EQMIXR also sums over the four input streams to get the moles of "non-equilibrium" solids, i.e.,

$$NT_{s,}(JNS) = NT_{s_R}(JNS) + NT_{c_L}(JNS) + NT_{f_L}(JNS) + NT_{w_M}(JNS) \qquad \text{(IV-9)}$$

where JNS is the index for non-equilibrium solids. These include CaO, MgO, $MgSO_4$, Na_2O, NaCl, and insoluble fly ash.

5. FILTER

This subroutine calculates stream vector quantities for the filter inlet (CB) stream and the filter liquid (FL) product stream based upon knowing stream vector information for the filter solids (FB) stream. The basic assumptions here are that essentially no chemical charge occurs within the filter and that the filter operates isothermally. The temperature of the filter and its process flow streams is fixed by the temperature of the FB stream.

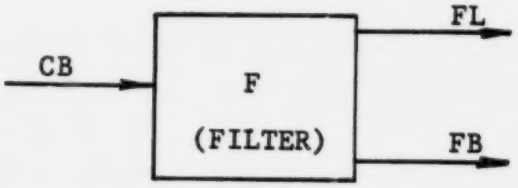

FIGURE IV-7

FILTER Flow Diagram

In addition to knowing the FB stream, the filter efficiency and weight fraction solids in the filter inlet (CB) stream are set by model inputs as equipment parameters. Since no chemical change occurs in the filter, the composition of the liquid phase for the CB and FL streams can be set equal to the liquid-phase composition of the FB stream. The relative amounts of the solid and liquid phases for the CB and FL streams are then determined by knowing the filter efficiency (XSOF) and the weight fraction solids in the CB stream (XWS_{CB}). That is,

$$L_{CB} = \frac{L_{FB}}{1-XSOF}\left(\frac{XWS_{FB}}{1-XWS_{FB}}\right)\left(\frac{1-XWS_{CB}}{XWS_{CB}}\right) \qquad \text{(IV-10)}$$

where L_{CB} and L_{FB} are the liquid flow rates of the CB and FB streams, respectively. Then,

$$L_{FL} = L_{CB} - L_{FB} \qquad \text{(IV-11)}$$

and

$$XWS_{FL} = \frac{XSOF * \left(\frac{XWS_{CB}}{1-XWS_{CB}}\right)\left(\frac{L_{CB}}{L_{FL}}\right)}{1 + XSOF * \left(\frac{XWS_{CB}}{1-XWS_{CB}}\right)\left(\frac{L_{CB}}{L_{FL}}\right)} \qquad \text{(IV-12)}$$

where L_{FL} is the liquid flow rate of the FL stream and XWS_{FL} is the weight fraction solids in FL.

The moles of solid species in the FL stream $[N_{FL}(JS)]$ are then calculated by the relation:

$$N_{FL}(JS) = \left(\frac{XWS_{FB} - XWS_{CB}}{XWS_{CB} - XWS_{FL}}\right)\left(\frac{XWS_{FL}}{XWS_{FB}}\right) N_{FB}(JS) \qquad \text{(IV-13)}$$

where the index JS refers to all solid species. Then,

$$N_{CB}(JS) = N_{FB}(JS) + N_{FL}(JS) \qquad \text{(IV-14)}$$

6. CLRFYR

This subroutine calculates the clarifier feed (CF) and clarifier liquid (CL) streams based upon the clarifier being a solid-liquid separator only and upon the clarifier bottoms (CB) stream being completely known. In this subroutine, the CF stream is determined by process parameters exterior to this routine. More specifically, the liquid flow rates of the scrubber feed (SF) and slurry recycle (SR) streams are required inputs for the CLRFYR subroutine. In addition, the amount of solids in the CL stream are set by a clarifier efficiency (XSOC).

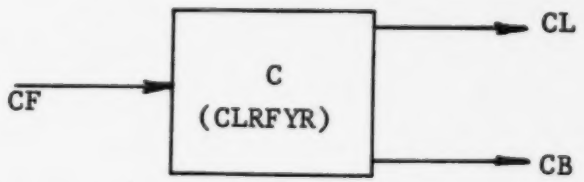

FIGURE IV-8

CLRFYR Flow Diagram

The CLRFYR subroutine is basically composed of two parts. The first part involves setting elements in the CF and CL stream vectors equal to the equivalent elements in the CB stream vector. The temperatures of the CF and CL streams are set equal to the CB temperatures. Since no chemical change is

assumed to occur within the clarifier, the liquid-phase compositions of CF and CL are set equal to those of CB.

The second part involves determining the amounts (L_{cf} and L_{cL}) of these two unknown streams. These amounts depend upon the systems iterative parameters L_{sf} and L_{sR} since the weight of liquid water is not strictly conserved about the process water hold tank. For example, the hydration of CaO to $Ca(OH)_2$ consumes liquid water. A total weight balance around the process water hold tank is not possible at this point since the compositions (and thus densities) of the SF and SR streams are unknown. The approach that has been used in the CLRFYR subroutine is (1) to make the rather good approximation that the moles of liquid water are conserved about the process water hold tank and then (2) to iterate to correct any error involved with this approximation. Thus for the first CLRFYR calculation

$$L^1_{cf} = L^\circ_{sf} + L_{fB} - L_{WM} - L_{sR} \qquad \text{(IV-15)}$$

$$L^1_{cL} = L^1_{cf} - L_{cB} \qquad \text{(IV-16)}$$

Based upon these values for L_{cf} and L_{cL}, the EQMIXR subroutine will subsequently determine a possibly different value for L_{sf}, say L^*_{sf}. At this point, control is returned to the CLRFYR subroutine and new values for L_{cf} and L_{cL} are determined by the relations

$$L^{(i+1)}_{cf} = L^{(i+1)}_{*} + L_{fB} - L_{WM} - L_{sR} \qquad \text{(IV-17)}$$

$$L^{(i+1)}_{cL} = L^{(i+1)}_{cf} - L_{cB} \qquad \text{(IV-18)}$$

where $L^{(i+1)}_{*}$ is an iterative parameter such that in the solution $L^*_{sf} = L^\circ_{sf}$.

Once $L_{c,}$ and L_{cL} have been determined the weight fraction solids ($XWS_{c,}$ and XWS_{cL}) and moles of each solid species [$N_{c,}(JS)$ and $N_{cL}(JS)$], in these two streams can be calculated as follows:

$$XWS_{c,} = \frac{\left(\frac{1}{1-XSOC}\right)\left(\frac{XWS_{cB}}{1-XWS_{cB}}\right)\left(\frac{L_{cB}}{L_{c,}}\right)}{1 + \left(\frac{1}{1-XSOC}\right)\left(\frac{XWS_{cB}}{1-XWS_{cB}}\right)\left(\frac{L_{cB}}{L_{c,}}\right)} \qquad \text{(IV-19)}$$

$$XWS_{cL} = \frac{(XSOC)\left(\frac{XWS_{c,}}{1-XWS_{c,}}\right)\left(\frac{L_{c,}}{L_{cL}}\right)}{1 + (XSOC)\left(\frac{XWS_{c,}}{1-XWS_{c,}}\right)\left(\frac{L_{c,}}{L_{cL}}\right)} \qquad \text{(IV-20)}$$

$$N_{cL}(JS) = \left(\frac{XWS_{cB} - XWS_{c,}}{XWS_{c,} - XWS_{cL}}\right) N_{cB}(JS) \qquad \text{(IV-21)}$$

$$N_{c,}(JS) = N_{cB}(JS) + N_{cL}(JS) \qquad \text{(IV-22)}$$

7. DIVDER

This subroutine determines the elements of the stream vector for the input stream and one output stream given the elements of the other output stream. This program is used in the prototype simulations to determine the effluent bottoms (EB) and slurry recycle (SR) streams once the clarifier feed (CF) stream is known.

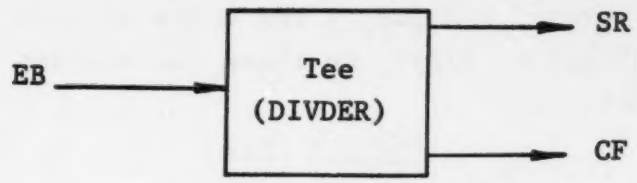

FIGURE IV-9

DIVDER Flow Diagram

In addition to knowing the CF stream completely, the liquid flow rate for the SR stream (L_{sR}) is also required as a subroutine input.

The program determines the size of the EB stream as the sum of the SR and CF stream, i.e.,

$$L_{tB} = L_{cF} + L_{sR} \qquad \text{(IV-23)}$$

and sets the compositions of the EB and SR stream equal to that of the CF stream. Thus, the program assumes no chemical change and no solid-liquid separation occurs within DIVDER.

8. OVALMB

This subroutine first uses an adiabatic humidification calculation for the scrubber to determine the amount of water vaporized and liquor temperature in the scrubber. Then, using this information along with a material balance for the overall system, OVALMB calculates the amounts and compositions of the filter bottoms (FB) and stack gas (SG) streams and the amount of water makeup (WM).

The diagram given below shows the solid-liquid stream leaving the system as being the filter bottoms (FB) stream.

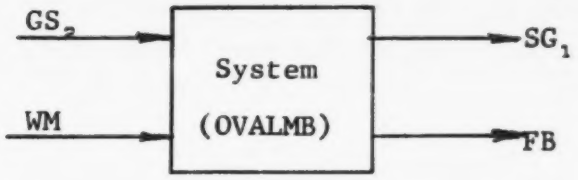

FIGURE IV-10

OVALMB Flow Diagram

For systems without a filter, this stream would of course be the clarifier bottoms (CB) stream.

The compositions of the gas-solid stream entering the scrubber (GS_2) and the water makeup (WM) are taken as known inputs to the subroutine. In addition, the fractions of (1) SO_2 and NO_x absorbed in the scrubber, (2) SO_2 oxidized in the scrubber, and (3) CaO and MgO hydrated in the system are also known. Two equipment parameters, pressure drop across the scrubber ($-\Delta P_s$) and weight fraction solids in the filter bottoms ($XWS_{F,B}$), are required inputs for OVALMB. For each iteration through the OVALMB subroutine, the fraction of CO_2 absorbed in the scrubber [$XA(CO_2)$] is also a fixed subroutine parameter.

The amount of water vaporized and the liquor temperature in the scrubber are calculated by the simultaneous solution of mass and energy balances about the scrubber. In the energy balance, the scrubber is assumed to be adiabatic. The heats of reaction, solution, etc., are neglected. The exit gas (SG_2) and liquid (SB) streams are assumed to reach the adiabatic

saturation temperature (T_{AS}) and temperature of the entering liquid (SF) is assumed to close enough to T_{AS} such that this sensible heat term can be neglected.

This phase of the OVALMB calculations is performed by the WAVAP subroutine. Here, the mass balance is written as Equation IV-24

$$N_{WV} = \frac{\left[N_{GS_2} - N_{GS_2}(H_2O) - \Delta N_{Abs}\right] * Y_{SG_1}(H_2O)}{1 - Y_{SG_1}(H_2O)} - N_{GS_2}(H_2O)$$

$$= \Phi_{MB}(T_{AS}) \qquad \text{(IV-24)}$$

In Equation IV-24 N_{WV} is the moles of water vaporized (unknown), N_{GS_2} is the total moles of GS_2, $N_{GS_2}(H_2O)$ is the moles of H_2O in GS_2, ΔN_{Abs} is the moles of gas species absorbed in the scrubber, $Y_{SG_1}(H_2O)$ is the mole fraction of H_2O in the stack gas stream and $\Phi_{MB}(T_{AS})$ represents the value of N_{WV} calculated by the mass balance. $Y_{SG_1}(H_2O)$ is a function of the temperature T_{AS}, i.e.,

$$Y_{SG_1}(H_2O) = \left(\frac{a_{H_2O}}{P_{SG_1}}\right) * 10^{5.22684-1750.286/(T_{AS}-38.2)} \qquad \text{(IV-25)}$$

The energy balance is given by Equation IV-26

$$N_{WV} = \frac{\left(Cp_{GS}\right)_{mean} * \left(T_{GS_2} - T_{AS}\right)}{\left(\Delta H_{vap}\right)_{T_{AS}}} = \Phi_{EB}(T_{AS}) \qquad \text{(IV-26)}$$

In Equation IV-26 $(Cp_{GS})_{mean}$ is the mean heat capacity of the GS_2 stream, T_{GS_2} is the temperature of the GS_2 stream, and $(\Delta H_{vap})_{T_{AS}}$ is the heat of vaporization for H_2O at the temperature T_{AS}. $(\Delta H_{vap})_{T_{AS}}$ is a function of temperature, i.e.,

$$(\Delta H_{vap})_{T_{AS}} = 13,630.6-10.464*T_{AS} \qquad \text{(IV-27)}$$

The quantity $\Phi_{FB}(T_{AS})$ is the value of N_{WV} calculated by the energy balance. The solution is the value of T_{AS} such that $\Phi_{MB} = \Phi_{FB}$. The WAVAP subroutine solves this problem numerically using a Newton-Raphson technique. The result is valued for N_{WV} and T_{AS}. The process liquor circulating in the system is assumed to have the temperature T_{AS}.

The moles of key species leaving the system in the filter bottoms (FB) stream can now be determined. Key-species in the FB stream come from three sources: (1) the gas species absorbed in the scrubber, (2) the solids from the limestone-fly ash streams, and (3) the water makeup, i.e.,

$$NT_{FB}(JT) = \Delta N_{AT}(JT) + N_{DT}(JT) + NT_{WM}(JT) \qquad \text{(IV-28)}$$

where $NT_{FB}(JT)$ and $NT_{WM}(JT)$ are the moles of the key species JT in the FB and WM streams. As in the SCRUBR routine, $\Delta N_{AT}(JT)$ is the moles of key species JT absorbed by the system from the flue gas. The term $N_{DT}(JT)$ represents the moles of key species JT that enter the system from the limestone-fly ash (LA) stream except for "inert" solids. These inert solids include the insoluble fly ash and the quantity of CaO and MgO that does not hydrate in the system.

Based upon the process model assumptions, the chemical species (excluding the unreactive portion of CaO and MgO) in the FB stream are in solid-liquid equilibrium at the temperature of the scrubbing liquid. Thus the Radian chemical equilibrium program can be used to calculate the composition of the FB stream. In this calculation, the moles of the first eight key species (SO_2, CO_2, SO_3, N_2O_5, CaO, MgO, Na_2O, and HCl) are calculated by Equation (IV-28). For the first calculation, the moles of water makeup (N_{WM}) are unknown so that the key species entering from this stream are neglected initially. Chemical equilibrium is then calculated using an option of the Radian program whereby the moles of the first eight key species plus the weight fraction solids are specified as program inputs. This version determines the resulting equilibrium composition and the moles of total H_2O species [$NT_{,s}(H_2O)$]. The moles of water makeup (N_{WM}) can then be determined by the relation:

$$N_{WM}(H_2O) = NT_{,s}(H_2O) + N_{WV} \qquad \text{(IV-29)}$$

where as before N_{WV} are the moles of water vaporized in the scrubber. An iteration loop is used to account for the water makeup species in Equation (IV-28).

9. Other Subroutines

As mentioned earlier subroutines for material sources (FLUGAS and WTRMKP) and sinks (STKGAS and FLTRBM) are also used by the Radian process model. These programs essentially read input data and convert them into usable units or prepare calculated data for output printing.

C. Convergence

Two major iteration loops are required to converge the simulation cases for the prototype LIWS system. First, a composition of the scrubber bottoms (SB) stream must be obtained such that the equilibrium vapor pressure of SO_2 for this stream is equal to the desired partial pressure of the stack gas (SG) stream. In this case, the amount of slurry recycle (SR) or scrubber feed (SF) is used as the iterative parameter for "SO_2 convergence". Secondly, the fraction of CO_2 absorbed by process [$XA(CO_2)$] is also assumed to be controlled by the equilibrium vapor pressure of CO_2 above the SB stream. The Radian process model assumes an initial value for $XA(CO_2)$ and then adjusts this parameter until the molality of total carbonate in the SB stream coincides with the molality required to give the CO_2 partial pressure of the stack gas.

The approach used to converge the prototype simulation cases is to iterate on SO_2 via a "loop" internal to the CO_2 convergence loop. This approach was chosen based upon the observations that (1) the molality of total CO_2 in SB will be essentially constant (corresponding closely to the partial pressure of CO_2 in the flue gas since a small fraction is absorbed) and (2) the $XA(CO_2)$ influences the OVALMB calculations.

Since the molality of total CO_2 in SB will not change significantly as $XA(CO_2)$ is varied, the values of slurry recycle (or scrubber feed) rates obtained by SO_2 convergence at one level of $XA(CO_2)$ will be relatively close to the SR rate at another $XA(CO_2)$ level.

The SO_2 convergence technique is a modified version of the Method of False Position* whereby a straight line interpolation is used to find the next SR (or SF) rate. The "poles" or known points are continually updated so as to use values closest to the solution. The logarithm of the SO_2 partial pressure is used in the straight line interpolation.

The CO_2 convergence routine uses a straight line relation between the moles of total CO_2 in the $SB[NT_{SB}(CO_2)]$ and the fraction of CO_2 absorbed from the flue gas, i.e.,

$$NT_{SB}(CO_2) = A * XA(CO_2) + B \qquad \text{(IV-31)}$$

Since A is known, one point is required to determine a new value of $XA(CO_2)$ for the next iteration.

The procedure used in the prototype simulations was to select an initial value for $XA(CO_2)$ and perform the simulation calculations to obtain values for $NT_{SB}(CO_2)$ and $NT^*_{SB}(CO_2)$. Here, $NT_{SB}(CO_2)$ corresponds to the value obtained from Equation (IV-30) and $NT^*_{SB}(CO_2)$ corresponds to the value obtained from the equilibrium calculation in the scrubber. To obtain the next iterative value for $XA(CO_2)$, $NT^*_{SB}(CO_2)$ is used in Equation (IV-30) and a value for $XA(CO_2)$ is calculated.

*Kunz, K. S., Numerical Analysis, McGraw-Hill Book Company, Inc., New York, 1957.

V. CONCLUDING REMARKS

Radian has developed a computerized process model for the LIWS process. The present model is based upon a number of process assumptions which reflect the current knowledge of process rate steps and equipment characteristics. Insofar as possible, the computerized system has been designed for flexibility so that a number of control schemes can be simulated. Specialization has been used when a significant improvement in computational time would result.

The present model represents a valuable tool to process development and design. The model could be significantly improved by including rate correlations when appropriate rate data become available.

APPENDIX

Example Simulation Case

(Prototype Simulation No. 2-B)

PROTOTYPE SIMULATION\NO. 2-B

PROCESS DESCRIPTION

EQUP. NO.	EQUIP.NAME	INPUT STREAMS				OUTPUT STREAMS	
1	FLUGAS	0				1	
2	WTRMKP	0				14	
3	CLRHTR	1				2	
4	SCRUBR	2	15			3	6
5	CLRHTR	3				4	
6	DIVDER	7				8	9
7	CLRFYR	9				10	11
8	FILTER	11				12	13
9	EQMIXR	8	10	12	14	15	
10	OVALMB	2	14			3	13
11	FLTRBM	13					
12	STKGAS	5					
13	PMPFAN	4				5	

ORDER OF PROCESS CALCULATIONS

1,2,3(10,8(7,6,9,4))5,11,13,12*

RECYCLE LOOP FROM 10 TO 4

RECYCLE LOOP FROM 7 TO 4

04 AUG 70 10:51:09.307 PROTOTYPE SIMULATION NO. 2-B

PROCESS CONDITIONS

FLUE GAS RATE = 100000.00 ACFM AT TFG = 275. DEG. F AND PFG = 14.7 PSIA

SO2 ABSORBED = 90.0 % NO ABSORBED = 10.00 %

SO2 OXIDIZED = 50.0 % NO2 ABSORBED = 100. %

LIMESTONE RATE = 31.4 LBS/MIN = 150. % THEORETICAL

LIMESTONE COMPOSITION = .000 MOLES (MG)/MOLES(CA+MG)

LIME REACTED IN BOILER = .000 %

NO PRECIPITATION ALLOWED IN SCRUBBER

LIME HYDRATED

IN SYSTEM

CAO = 75.0 %

MGO = 75.0 %

IN SCRUBBER

CAO = 20.0 %

MGO = 20.0 %

SOLIDS DISSOLVED IN SCRUBBER

	LA	SF
CA(OH)2 =	40.0 %	35.0 %
MG(OH)2 =	40.0 %	35.0 %
CACO3 =	40.0 %	35.0 %
MGCO3 =	40.0 %	35.0 %
MGSO4 =	40.0 %	35.0 %
NA2O =	40.0 %	35.0 %
NACL =	40.0 %	35.0 %

FLY ASH RATE = 40.0 LBS/MIN = 3.35 LBS FA/LB SULFUR IN COAL

EQUIPMENT PARAMETERS;

SOLIDS IN CLARIFIER BOTTOMS = 30.0 WT.% CLARIFIER EFFICIENCY = 99.0 %

SOLIDS IN FILTER BOTTOMS = 60.0 WT.% FILTER EFFICIENCY = 99.0 %

TEMP. OF COOLED G-S STREAM = 225. DEG F TEMP. OF REHEATED STACK GAS = 250. DEG. F

I.D. FAN EXIT PRESSURE = 14.7 PSIA

UNIT PRESSURE LOSSES, PSIA

COOLER = .144 SCRUBBER = .288 REHEATER = .144

INITIAL VALUES ;

SCRUBBER FEED RATE = 14.0 GPM H2O SF/1000 ACFM FG = 1400.00 GPM H2O

INPUT STREAM COMPOSITIONS ;

FLUE GAS

COMP.	MOLE %
SO2 =	.200
CO2 =	14.5
NO =	.450-01
NO2 =	.500-02
O2 =	3.00
CO =	.000
N2 =	74.2
HCL =	.000
H2O =	8.00

LIMESTONE

COMP.	WT.%
CAO =	100.
MGO =	.000
CACO3 =	.000
MGCO3 =	.000
CASO3 =	.000
MGSO3 =	.000
CASO4 =	.000
MGSO4 =	.000

FLY ASH

COMP.	WT.%
NA2O =	.112
NACL =	.746
INSOLUBLE FLY ASH =	99.1

WATER MAKEUP

COMP.	MG/L
SO3 =	.000
CO3 =	.000
SO4 =	.000
NO3 =	.000
CA =	.000
MG =	.000
NA =	.000
CL =	.000

TEMPERATURE 48.791 DEGREES C

EQUILIBRIUM CONSTANTS

REACTANT	K(25 C)	K(TEMP)	A	B	C	D
H2O	1.0129-14	5.1028-14	4.4710+03	0.0000	1.7060-02	6.0875+00
H2SO3	1.2957-02	8.0056-03	-8.4367+02	0.0000	0.0000	-4.7171+00
HSO3	6.2207-08	4.3326-08	-6.3384+02	0.0000	0.0000	-9.3320+00
HSO4	1.0396-02	5.0245-03	4.7514+02	0.0000	1.8222-02	5.0435+00
H2CO3	4.4513-07	5.1559-07	3.4047+03	0.0000	3.2786-02	1.4843+01
HCO3	4.6817-11	6.6642-11	2.9024+03	0.0000	2.3790-02	6.4980+00
CAOH+	4.2229-02	3.6137-02	-2.7300+02	0.0000	0.0000	-2.2900+00
CASO3	3.9999-04	2.9988-04	-5.0480+02	0.0000	0.0000	-5.0910+00
CACO3	6.2996-04	4.8025-04	-4.7548+02	0.0000	0.0000	-4.7954+00
CAHCO3+	5.5002-02	4.6298-02	-3.0185+02	0.0000	0.0000	-2.2720+00
CASO4	4.8969-03	3.5939-03	2.5721+03	2.3150+01	0.0000	6.3600+01
CANO3+	4.8485-01	2.3826-01	-1.2450+03	0.0000	0.0000	-4.4900+00
CACO3(S)	4.8695-09	1.8883-09	-1.6600+03	0.0000	0.0000	-1.3880+01
CASO4(S)	2.4000-05	1.7433-05	4.9440+03	3.7745+01	0.0000	1.0530+02
CASO3(S)	8.4004-08	8.4004-08	0.0000	0.0000	0.0000	-7.0757+00
CA(OH)2(S)	5.6287-06	3.4099-06	7.6560+02	4.4700-07	1.7125-02	2.4240+00
MGOH+	2.6001-03	1.9347-03	-5.1799+02	0.0000	0.0000	-4.3223+00
MGSO3	1.1997-03	9.3729-04	-4.3250+02	0.0000	0.0000	-4.3715+00
MGHCO3+	1.1001-01	9.6200-02	-2.3508+02	0.0000	0.0000	-1.7470+00
MGSO4	5.6636-03	3.0967-03	-1.0579+03	0.0000	0.0000	-5.7950+00
MGCO3	3.9999-04	2.9988-04	-5.0480+02	0.0000	0.0000	-5.0910+00
MG(OH)2(S)	1.2552-11	9.5400-12	-4.6085+02	0.0000	0.0000	-1.2514+01
MGSO3(S)	5.3272-05	5.9144-05	8.0220+02	0.0000	0.0000	-1.5830+00
MGCO3(S)	2.1500-05	1.2466-05	-9.5514+02	0.0000	0.0000	-7.8710+00
NAOH	3.7154+00	3.7154+00	0.0000	0.0000	0.0000	5.7000-01
NACO3-	5.4002-02	4.5416-02	-3.0341+02	0.0000	0.0000	-2.2852+00
NAHCO3	1.7783+00	1.7783+00	0.0000	0.0000	0.0000	2.5000-01
NASO4-	1.9024-01	1.6579-01	-2.4100+02	0.0000	0.0000	-1.5290+00
NANO3	2.5119+00	2.5119+00	0.0000	0.0000	0.0000	4.0000-01
PP(SO2)	1.2158+00	5.5630-01	-1.3700+03	0.0000	0.0000	-4.5100+00
PP(CO2)	3.4215-02	1.9171-02	-1.0150+03	0.0000	0.0000	-4.8700+00

HYDRATES IF PRECIPITATED ARE MGCO3*3H2O, MGSO3*3H2O, CASO3*(1/2)H2O

THIS PROGRAM DEVELOPED BY RADIAN CORP. UNDER NAPCA/HEW SPONSORSHIP

04 AUG 70 10:53:26.103 PROTOTYPE SIMULATION NO. 2-B

STREAM NUMBER		1	2	3	4	5	6
TOTAL STREAM							
FLOW RATE	(G/SEC)	42437.	42437.	42739.	42739.	42739.	92034.
	(G-MOLE/SEC)	1417.6	1417.6	1463.3	1463.3	1463.3	4868.4
TEMPERATURE	(DEG. K)	408.16	360.38	321.95	394.27	394.27	321.95
PRESSURE	(ATM)	1.0000	.99020	.97060	.96081	1.0000	.00000
ENTHALPY	(CAL/SEC)	-.26356+08	-.26653+08	-.28788+08	-.28000+08	-.28000+08	-.33736+09
SOLIDS	(WT %)	1.2718	1.2718	.00000	.00000	.00000	2.6401
GAS PHASE							
FLOW RATE	(G/SEC)	41898.	41898.	42739.	42739.	42739.	.00000
	(G-MOLE/SEC)	1409.3	1409.3	1463.3	1463.3	1463.3	.00000
ENTHALPY	(CAL/SEC)	-.24761+08	-.25055+08	-.28788+08	-.28000+08	-.28000+08	.00000
COMP	(G-MOLES/SEC)						
SO2		2.8187	2.8187	.28187	.28187	.28187	.00000
CO2		204.35	204.35	204.25	204.25	204.25	.00000
NO		.63420	.63420	.57078	.57078	.57078	.00000
NO2		.70467-01	.70467-01	.00000	.00000	.00000	.00000
O2		42.280	42.280	41.581	41.581	41.581	.00000
CO		.00000	.00000	.00000	.00000	.00000	.00000
N2		1046.4	1046.4	1046.4	1046.4	1046.4	.00000
HCL		.00000	.00000	.00000	.00000	.00000	.00000
H2O		112.75	112.75	170.23	170.23	170.23	.00000
LIQUID PHASE							
FLOW RATE	(G/SEC)	.00000	.00000	.00000	.00000	.00000	89604.
	(G-MOLES/SEC)	.00000	.00000	.00000	.00000	.00000	4839.7
ENTHALPY	(CAL/SEC)	.00000	.00000	.00000	.00000	.00000	-.33042+09
COMP	(G-MOLES/SEC)						
SO2		.00000	.00000	.00000	.00000	.00000	1.2925
CO2		.00000	.00000	.00000	.00000	.00000	.20587
SO3		.00000	.00000	.00000	.00000	.00000	2.1138
N2O5		.00000	.00000	.00000	.00000	.00000	12.099
CAO		.00000	.00000	.00000	.00000	.00000	13.884
MGO		.00000	.00000	.00000	.00000	.00000	.00000
NA2O		.00000	.00000	.00000	.00000	.00000	4.4629
HCL		.00000	.00000	.00000	.00000	.00000	6.9539
H2O		.00000	.00000	.00000	.00000	.00000	4798.7
DENSITY	(G/ML AT T)	.00000	.00000	.00000	.00000	.00000	1.0209
IONIC STRENGTH		.00000	.00000	.00000	.00000	.00000	.51387
PH		.00000	.00000	.00000	.00000	.00000	4.0588

04 AUG 70 10:53:26.346 PROTOTYPE SIMULATION NO. 2-B

STREAM NUMBER	1	2	3	4	5	6
LIQ. H2O RATE (KG/SEC)	.00000	.00000	.00000	.00000	.00000	86.501
COMP (G-MOLES/KG H2O)						
H+	.00000	.00000	.00000	.00000	.00000	.97427-04
OH-	.00000	.00000	.00000	.00000	.00000	.79750-09
HSO3-	.00000	.00000	.00000	.00000	.00000	.14398-01
SO3=	.00000	.00000	.00000	.00000	.00000	.25607-04
SO4=	.00000	.00000	.00000	.00000	.00000	.11938-01
HCO3-	.00000	.00000	.00000	.00000	.00000	.23158-04
CO3=	.00000	.00000	.00000	.00000	.00000	.63350-10
NO3-	.00000	.00000	.00000	.00000	.00000	.25515
HSO4-	.00000	.00000	.00000	.00000	.00000	.36638-04
H2SO3(L)	.00000	.00000	.00000	.00000	.00000	.93813-04
H2CO3(L)	.00000	.00000	.00000	.00000	.00000	.23428-02
CA++	.00000	.00000	.00000	.00000	.00000	.12709
CAOH+	.00000	.00000	.00000	.00000	.00000	.65864-09
CASO3(L)	.00000	.00000	.00000	.00000	.00000	.42448-03
CACO3(L)	.00000	.00000	.00000	.00000	.00000	.65568-09
CAHCO3+)	.00000	.00000	.00000	.00000	.00000	.13491-04
CASO4(L)	.00000	.00000	.00000	.00000	.00000	.11565-01
CANO3+	.00000	.00000	.00000	.00000	.00000	.21414-01
MG++	.00000	.00000	.00000	.00000	.00000	.00000
MGOH+	.00000	.00000	.00000	.00000	.00000	.00000
MGSO3(L)	.00000	.00000	.00000	.00000	.00000	.00000
MGHCO3+	.00000	.00000	.00000	.00000	.00000	.00000
MGSO4(L)	.00000	.00000	.00000	.00000	.00000	.00000
MGCO3(L)	.00000	.00000	.00000	.00000	.00000	.00000
NA+	.00000	.00000	.00000	.00000	.00000	.99114-01
NAOH(L)	.00000	.00000	.00000	.00000	.00000	.10016-10
NACO3-	.00000	.00000	.00000	.00000	.00000	.24827-10
NAHCO3(L)	.00000	.00000	.00000	.00000	.00000	.54915-06
NASO4-	.00000	.00000	.00000	.00000	.00000	.89767-03
NANO3-	.00000	.00000	.00000	.00000	.00000	.31757-02
CL-	.00000	.00000	.00000	.00000	.00000	.80391-01
SOLID PHASE						
FLOW RATE (G/SEC)	539.73	539.73	.00000	.00000	.00000	2429.8
(G-MOLES/SEC)	8.2302	8.2302	.00000	.00000	.00000	28.714
ENTHALPY (CAL/SEC)	-.15944+07	-.15974+07	.00000	.00000	.00000	-.69394+07

04 AUG 70 10:53:26.584 PROTOTYPE SIMULATION NO. 2-B

STREAM NUMBER	1	2	3	4	5	6
COMP (G-MOLES/SEC)						
CAO	4.2279	4.2279	.00000	.00000	.00000	6.3694
CA(OH)2	.00000	.00000	.00000	.00000	.00000	1.1494
CACO3	.00000	.00000	.00000	.00000	.00000	.18278
CASO3	.00000	.00000	.00000	.00000	.00000	.00000
CASO3*1/2H2O	.00000	.00000	.00000	.00000	.00000	3.3302
CASO4	.00000	.00000	.00000	.00000	.00000	3.3025
CASO4*2H2O	.00000	.00000	.00000	.00000	.00000	.00000
MGO	.00000	.00000	.00000	.00000	.00000	.00000
MG(OH)2	.00000	.00000	.00000	.00000	.00000	.00000
MGCO3	.00000	.00000	.00000	.00000	.00000	.00000
MGCO3*3H2O	.00000	.00000	.00000	.00000	.00000	.00000
MGCO3*5H2O	.00000	.00000	.00000	.00000	.00000	.00000
MGSO3	.00000	.00000	.00000	.00000	.00000	.00000
MGSO3*3H2O	.00000	.00000	.00000	.00000	.00000	.00000
MGSO3*6H2O	.00000	.00000	.00000	.00000	.00000	.00000
MGSO4	.00000	.00000	.00000	.00000	.00000	.00000
NA2O	.54735-02	.54735-02	.00000	.00000	.00000	.32841-02
INSOLUBLE FLY ASH	3.9582	3.9582	.00000	.00000	.00000	14.353
NACL	.38605-01	.38605-01	.00000	.00000	.00000	.23163-01
SUMMARY IN ENGINEERING UNITS						
TOT FLOW RATE (LBS/MIN)	5613.4	5613.4	5653.2	5653.2	5653.2	12174.
(LB-MOLES/MIN)	187.51	187.51	193.56	193.56	193.56	643.97
GAS FLOW RATE (LBS/MIN)	5542.0	5542.0	5653.2	5653.2	5653.2	.00000
(LB-MOLES/MIN)	186.42	186.42	193.56	193.56	193.56	.00000
(ACFM)	100000.					.00000
LIQ FLOW RATE (LBS/MIN)	.00000	.00000	.00000	.00000	.00000	11852.
(LB-MOLES/MIN)	.00000	.00000	.00000	.00000	.00000	640.18
(1000 LBS H2O/MIN)	.00000	.00000	.00000	.00000	.00000	11.442
(GAL/MIN)	.00000	.00000	.00000	.00000	.00000	1386.9
LIQ DENSITY (LBS/GAL@T)	.00000	.00000	.00000	.00000	.00000	8.5198
SOL FLOW RATE (LBS/MIN)	71.392	71.392	.00000	.00000	.00000	321.41
(LB-MOLES/MIN)	1.0886	1.0886	.00000	.00000	.00000	3.7981

04 AUG 70 10:53:27.010 PROTOTYPE SIMULATION NO. 2-B

STREAM NUMBER		7	8	9	10	11	12
TOTAL STREAM							
FLOW RATE	(G/SEC)	92035.	66139.	25896.	23401.	2495.2	1260.9
	(G-MOLE/SEC)	4864.6	3495.8	1368.8	1266.0	102.78	67.911
TEMPERATURE	(DEG. K)	321.95	321.95	321.95	321.95	321.95	321.95
PRESSURE	(ATM)	.00000	.00000	.00000	.00000	.00000	.00000
ENTHALPY	(CAL/SEC)	-.33743+09	-.24248+09	-.94943+08	-.86383+08	-.85606+07	-.46485+07
SOLIDS	(WT %)	2.9151	2.9151	2.9151	.32259-01	29.951	.59269
GAS PHASE							
FLOW RATE	(G/SEC)	.00000	.00000	.00000	.00000	.00000	.00000
	(G-MOLE/SEC)	.00000	.00000	.00000	.00000	.00000	.00000
ENTHALPY	(CAL/SEC)	.00000	.00000	.00000	.00000	.00000	.00000
COMP	(G-MOLES/SEC)						
SO2		.00000	.00000	.00000	.00000	.00000	.00000
CO2		.00000	.00000	.00000	.00000	.00000	.00000
NO		.00000	.00000	.00000	.00000	.00000	.00000
NO2		.00000	.00000	.00000	.00000	.00000	.00000
O2		.00000	.00000	.00000	.00000	.00000	.00000
CO		.00000	.00000	.00000	.00000	.00000	.00000
N2		.00000	.00000	.00000	.00000	.00000	.00000
HCL		.00000	.00000	.00000	.00000	.00000	.00000
H2O		.00000	.00000	.00000	.00000	.00000	.00000
LIQUID PHASE							
FLOW RATE	(G/SEC)	89352.	64211.	25142.	23394.	1747.9	1253.5
	(G-MOLES/SEC)	4835.1	3474.6	1360.5	1265.9	94.583	67.829
ENTHALPY	(CAL/SEC)	-.32986+09	-.23704+09	-.92814+08	-.86362+08	-.84525+07	-.46274+07
COMP	(G-MOLES/SEC)						
SO2		.23789-01	.17096-01	.66937-02	.62284-02	.46535-03	.33372-03
CO2		.35826-03	.25745-03	.10081-03	.93798-04	.70081-05	.50258-05
SO3		.83364	.59907	.23457	.21826	.16307-01	.11695-01
N2O5		12.099	8.6944	3.4043	3.1676	.23667	.16973
CAO		13.151	9.4509	3.7005	3.4432	.25726	.18449
MGO		.00000	.00000	.00000	.00000	.00000	.00000
NA2O		4.4778	3.2178	1.2599	1.1723	.87592-01	.62816-01
HCL		6.9771	5.0139	1.9632	1.8267	.13648	.97877-01
H2O		4797.6	3447.7	1349.9	1256.1	93.848	67.302
DENSITY	(G/ML AT T)	1.0184	1.0184	1.0184	1.0184	1.0184	1.0184
IONIC STRENGTH		.48277	.48277	.48277	.48277	.48277	.48277
PH		11.344	11.344	11.344	11.344	11.344	11.344

04 AUG 70 10:53:27.261 PROTOTYPE SIMULATION NO. 2-B

STREAM NUMBER	7	8	9	10	11	12
LIQ. H2O RATE (KG/SEC)	86.475	62.143	24.332	22.640	1.6916	1.2131
COMP (G-MOLES/KG H2O)						
H+	.51089-11	.51089-11	.51089-11	.51089-11	.51089-11	.51089-11
OH-	.15467-01	.15467-01	.15467-01	.15467-01	.15467-01	.15467-01
HSO3-	.49008-09	.49008-09	.49008-09	.49008-09	.49008-09	.49008-09
SO3=	.16481-04	.16481-04	.16481-04	.16481-04	.16481-04	.16481-04
SO4=	.48039-02	.48039-02	.48039-02	.48039-02	.48039-02	.48039-02
HCO3-	.71292-08	.71292-08	.71292-08	.71292-08	.71292-08	.71292-08
CO3=	.36877-06	.36877-06	.36877-06	.36877-06	.36877-06	.36877-06
NO3-	.25633	.25633	.25633	.25633	.25633	.25633
HSO4-	.79571-12	.79571-12	.79571-12	.79571-12	.79571-12	.79571-12
H2SO3(L)	.16763-18	.16763-18	.16763-18	.16763-18	.16763-18	.16763-18
H2CO3(L)	.37864-13	.37864-13	.37864-13	.37864-13	.37864-13	.37864-13
CA++	.11545	.11545	.11545	.11545	.11545	.11545
CAOH+	.11723-01	.11723-01	.11723-01	.11723-01	.11723-01	.11723-01
CASO3(L)	.25862-03	.25862-03	.25862-03	.25862-03	.25862-03	.25862-03
CACO3(L)	.36133-05	.36133-05	.36133-05	.36133-05	.36133-05	.36133-05
CAHCO3+)	.38445-08	.38445-08	.38445-08	.38445-08	.38445-08	.38445-08
CASO4(L)	.44577-02	.44577-02	.44577-02	.44577-02	.44577-02	.44577-02
CANO3+	.20192-01	.20192-01	.20192-01	.20192-01	.20192-01	.20192-01
MG++	.00000	.00000	.00000	.00000	.00000	.00000
MGOH+	.00000	.00000	.00000	.00000	.00000	.00000
MGSO3(L)	.00000	.00000	.00000	.00000	.00000	.00000
MGHCO3+	.00000	.00000	.00000	.00000	.00000	.00000
MGSO4(L)	.00000	.00000	.00000	.00000	.00000	.00000
MGCO3(L)	.00000	.00000	.00000	.00000	.00000	.00000
NA+	.99689-01	.99689-01	.99689-01	.99689-01	.99689-01	.99689-01
NAOH(L)	.19639-03	.19639-03	.19639-03	.19639-03	.19639-03	.19639-03
NACO3-	.14974-06	.14974-06	.14974-06	.14974-06	.14974-06	.14974-06
NAHCO3(L)	.17239-09	.17239-09	.17239-09	.17239-09	.17239-09	.17239-09
NASO4-	.37868-03	.37868-03	.37868-03	.37868-03	.37868-03	.37868-03
NANO3-	.32986-02	.32986-02	.32986-02	.32986-02	.32986-02	.32986-02
CL-	.80684-01	.80684-01	.80684-01	.80684-01	.80684-01	.80684-01
SOLID PHASE						
FLOW RATE (G/SEC)	2682.9	1928.0	754.89	7.5489	747.35	7.4735
(G-MOLES/SEC)	29.420	21.142	8.2780	.82780-01	8.1953	.81953-01
ENTHALPY (CAL/SEC)	-.75678+07	-.54384+07	-.21294+07	-21294.	-.21081+07	-21081.

04 AUG 70 10:53:27.543 PROTOTYPE SIMULATION NO. 2-B

STREAM NUMBER	7	8	9	10	11	12
COMP (G-MOLES/SEC)						
CAO	3.9327	2.7543	1.0784	.10784-01	1.0676	.10676-01
CA(OH)2	1.6644	1.1961	.46833	.46833-02	.46364	.46364-02
CACO3	.38829	.27903	.10925	.10925-02	.10816	.10816-02
CASO3	.00000	.00000	.00000	.00000	.00000	.00000
CASO3•1/2H2O	4.5989	3.3049	1.2940	.12940-01	1.2811	.12811-01
CASO4	4.5826	3.2932	1.2894	.12894-01	1.2766	.12766-01
CASO4•2H2O	.00000	.00000	.00000	.00000	.00000	.00000
MGO	.00000	.00000	.00000	.00000	.00000	.00000
MG(OH)2	.00000	.00000	.00000	.00000	.00000	.00000
MGCO3	.00000	.00000	.00000	.00000	.00000	.00000
MGCO3•3H2O	.00000	.00000	.00000	.00000	.00000	.00000
MGCO3•5H2O	.00000	.00000	.00000	.00000	.00000	.00000
MGSO3	.00000	.00000	.00000	.00000	.00000	.00000
MGSO3•3H2O	.00000	.00000	.00000	.00000	.00000	.00000
MGSO3•6H2O	.00000	.00000	.00000	.00000	.00000	.00000
MGSO4	.00000	.00000	.00000	.00000	.00000	.00000
NA2O	.00000	.00000	.00000	.00000	.00000	.00000
INSOLUBLE FLY ASH	14.353	10.314	4.0386	.40386-01	3.9982	.39982-01
NACL	.00000	.00000	.00000	.00000	.00000	.00000
SUMMARY IN ENGINEERING UNITS						
TOT FLOW RATE (LBS/MIN)	12174.	8748.5	3425.5	3095.4	330.05	166.79
(LB-MOLES/MIN)	643.46	462.41	181.05	167.46	13.595	8.9630
GAS FLOW RATE (LBS/MIN)	.00000	.00000	.00000	.00000	.00000	.00000
(LB-MOLES/MIN)	.00000	.00000	.00000	.00000	.00000	.00000
(ACFM)	.00000	.00000	.00000	.00000	.00000	.00000
LIQ FLOW RATE (LBS/MIN)	11819.	8493.5	3325.6	3094.4	231.20	165.80
(LB-MOLES/MIN)	639.57	459.61	179.96	167.45	12.511	8.9721
(1000 LBS H2O/MIN)	11.438	8.2199	3.2185	2.9948	.22375	.16046
(GAL/MIN)	1386.5	996.37	390.13	363.00	27.122	19.450
LIQ DENSITY (LBS/GALAT)	8.4983	8.4983	8.4983	8.4983	8.4983	8.4983
SOL FLOW RATE (LBS/MIN)	354.88	255.02	99.854	.99854	98.855	.98855
(LB-MOLES/MIN)	3.8915	2.7965	1.0950	.10950-01	1.0840	.10840-01

STREAM NUMBER	13	14	15
LIQ. H2O RATE (KG/SEC)	.47847	1.5336	87.530
COMP (G-MOLES/KG H2O)			
H+	.51089-11	.22603-06	.50914-11
OH-	.15467-01	.22603-06	.15567-01
HSO3-	.49008-09	.00000	.49231-09
SO3=	.16481-04	.00000	.16576-04
SO4=	.48039-02	.00000	.48182-02
HCO3-	.71292-08	.00000	.71620-08
CO3=	.36877-06	.00000	.37091-06
NO3-	.25633	.00000	.25199
HSO4-	.79571-12	.00000	.80098-12
H2SO3(L)	.16763-18	.00000	.16788-18
H2CO3(L)	.37864-13	.00000	.37923-13
CA++	.11545	.00000	.11377
CAOH+	.11723-01	.00000	.11658-01
CASO3(L)	.25862-03	.00000	.25893-03
CACO3(L)	.36133-05	.00000	.36179-05
CAHCO3+)	.38445-08	.00000	.38236-08
CASO4(L)	.44577-02	.00000	.44034-02
CANO3+	.20192-01	.00000	.19717-01
MG++	.00000	.00000	.00000
MGOH+	.00000	.00000	.00000
MGSO3(L)	.00000	.00000	.00000
MGHCO3+	.00000	.00000	.00000
MGSO4(L)	.00000	.00000	.00000
MGCO3(L)	.00000	.00000	.00000
NA+	.99689-01	.00000	.97969-01
NAOH(L)	.19639-03	.00000	.19451-03
NACO3-	.14974-06	.00000	.14907-06
NAHCO3(L)	.17239-09	.00000	.17076-09
NASO4-	.37868-03	.00000	.37700-03
NANO3-	.32986-02	.00000	.32080-02
CL-	.80684-01	.00000	.79270-01
SOLID PHASE			
FLOW RATE (G/SEC)	739.87	.00000	1939.0
(G-MOLES/SEC)	8.1133	.00000	21.267
ENTHALPY (CAL/SEC)	-.20870+07	.00000	

04 AUG 70 10:53:27.907 PROTOTYPE SIMULATION NO. 2-8

STREAM NUMBER		13	14	15
TOTAL STREAM				
FLOW RATE	(G/SEC)	1234.3	1533.6	92334.
	(G-MOLE/SEC)	34.867	85.122	4914.9
TEMPERATURE	(DEG. K)	321.95	321.95	321.95
PRESSURE	(ATM)	.00000	.00000	.00000
ENTHALPY	(CAL/SEC)	-.39122+07	-.57787+07	
SOLIDS	(WT %)	59.944	.00000	2.1000
GAS PHASE				
FLOW RATE	(G/SEC)	.00000	.00000	.00000
	(G-MOLE/SEC)	.00000	.00000	.00000
ENTHALPY	(CAL/SEC)	.00000	.00000	.00000
COMP	(G-MOLES/SEC)			
SO2		.00000	.00000	.00000
CO2		.00000	.00000	.00000
NO		.00000	.00000	.00000
NO2		.00000	.00000	.00000
O2		.00000	.00000	.00000
CO		.00000	.00000	.00000
N2		.00000	.00000	.00000
HCL		.00000	.00000	.00000
H2O		.00000	.00000	.00000
LIQUID PHASE				
FLOW RATE	(G/SEC)	494.40	1533.6	90395.
	(G-MOLES/SEC)	26.753	85.122	4893.6
ENTHALPY	(CAL/SEC)	-.18251+07	-.57787+07	-.33382+09
COMP	(G-MOLES/SEC)			
SO2		.13163-03	.00000	.24115-01
CO2		.19823-05	.00000	.36316-03
SO3		.46126-02	.00000	.84541
N2O5		.66944-01	.00000	12.032
CAO		.72768-01	.00000	13.118
MGO		.00000	.00000	.00000
NA2O		.24776-01	.00000	4.4530
HCL		.38605-01	.00000	6.9385
H2O		26.546	85.122	4856.2
DENSITY	(G/ML AT T)	1.0184	.98861	1.0179
IONIC STRENGTH		.48277	.22603-05	.47548
PH		11.344	6.6461	11.346

04 AUG 70 10:53:27.907 PROTOTYPE SIMULATION NO. 2-B

STREAM NUMBER		13	14	15
TOTAL STREAM				
FLOW RATE	(G/SEC)	1234.3	1533.6	92334.
	(G-MOLE/SEC)	34.867	85.122	4914.9
TEMPERATURE	(DEG. K)	321.95	321.95	321.95
PRESSURE	(ATM)	.00000	.00000	.00000
ENTHALPY	(CAL/SEC)	-.39122+07	-.57787+07	
SOLIDS	(WT %)	59.944	.00000	2.1000
GAS PHASE				
FLOW RATE	(G/SEC)	.00000	.00000	.00000
	(G-MOLE/SEC)	.00000	.00000	.00000
ENTHALPY	(CAL/SEC)	.00000	.00000	.00000
COMP	(G-MOLES/SEC)			
SO2		.00000	.00000	.00000
CO2		.00000	.00000	.00000
NO		.00000	.00000	.00000
NO2		.00000	.00000	.00000
O2		.00000	.00000	.00000
CO		.00000	.00000	.00000
N2		.00000	.00000	.00000
HCL		.00000	.00000	.00000
H2O		.00000	.00000	.00000
LIQUID PHASE				
FLOW RATE	(G/SEC)	494.40	1533.6	90395.
	(G-MOLES/SEC)	26.753	85.122	4893.6
ENTHALPY	(CAL/SEC)	-.18251+07	-.57787+07	-.33382+09
COMP	(G-MOLES/SEC)			
SO2		.13163-03	.00000	.24115-01
CO2		.19823-05	.00000	.36316-03
SO3		.46126-02	.00000	.84541
N2O5		.66944-01	.00000	12.032
CAO		.72768-01	.00000	13.118
MGO		.00000	.00000	.00000
NA2O		.24776-01	.00000	4.4530
HCL		.38605-01	.00000	6.9385
H2O		26.546	85.122	4856.2
DENSITY	(G/ML AT T)	1.0184	.98861	1.0179
IONIC STRENGTH		.48277	.22603-06	.47548
PH		11.344	6.6461	11.346

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04 AUG 70 10:53:28.259 PROTOTYPE SIMULATION NO. 2-8

STREAM NUMBER	13	14	15
COMP (G-MOLES/SEC)			
CAO	1.0570	.00000	2.7757
CA(OH)2	.45901	.00000	1.1829
CACO3	.10708	.00000	.28120
CASO3	.00000	.00000	.00000
CASO3*1/2H2O	1.2683	.00000	3.3302
CASO4	1.2638	.00000	3.3025
CASO4*2H2O	.00000	.00000	.00000
MGO	.00000	.00000	.00000
MG(OH)2	.00000	.00000	.00000
MGCO3	.00000	.00000	.00000
MGCO3*3H2O	.00000	.00000	.00000
MGCO3*5H2O	.00000	.00000	.00000
MGSO3	.00000	.00000	.00000
MGSO3*3H2O	.00000	.00000	.00000
MGSO3*6H2O	.00000	.00000	.00000
MGSO4	.00000	.00000	.00000
NA2O	.00000	.00000	.00000
INSOLUBLE FLY ASH	3.9582	.00000	10.395
NACL	.00000	.00000	.00000
SUMMARY IN ENGINEERING UNITS			
TOT FLOW RATE (LBS/MIN)	163.26	202.85	12214.
(LB-MOLES/MIN)	4.6120	11.259	650.11
GAS FLOW RATE (LBS/MIN)	.00000	.00000	.00000
(LB-MOLES/MIN)	.00000	.00000	.00000
(ACFM)	.00000	.00000	.00000
LIQ FLOW RATE (LBS/MIN)	65.396	202.85	11957.
(LB-MOLES/MIN)	3.5388	11.259	647.30
(1000 LBS H2O/MIN)	.63290-01	.20285	11.578
(GAL/MIN)	7.6716	24.588	1403.4
LIQ DENSITY (LBS/GAL@T)	8.4983	8.2499	8.4943
SOL FLOW RATE (LBS/MIN)	97.867	.00000	256.49
(LB-MOLES/MIN)	1.0732	.00000	2.8131

04 AUG 70 10:53:28.411 PROTOTYPE SIMULATION NO. 2-B

EQUIPMENT OUTPUTS

I.D. FAN POWER REQUIEMENTS:
HORSEPOWER = 3.0868+02 KILOWATTS = 2.3019+02
COOLER/REHEATER:
Cooler HEAT DUTY =-297063.75CAL/SEC
Reheater HEAT DUTY = 787983.51CAL/SEC

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TECHNICAL NOTE 200-004-21

EQUILIBRIUM CALCULATIONS FOR TYPE I APCO INHOUSE EXPERIMENTS

11 March 1971

Prepared by:

James L. Phillips

CHEMICAL RESEARCH • SYSTEMS ANALYSIS • COMPUTER SCIENCE • CHEMICAL ENGINEERING

1.0 INTRODUCTION

This technical note gives the results of equilibrium calculations made during analysis of data from APCO's inhouse SO_2 scrubbing experiments. These experiments were conducted at the Division of Process Control Engineering's Cincinnati laboratory facilities during the period August to December, 1970.

2.0 EXPERIMENTAL APPROACH

The test program for the Type I experiments was described in detail in Radian Technical Note 200-002-05. The primary purpose of this experimental series was to observe the approach to vapor-liquid equilibrium in a venturi scrubber during SO_2 absorption. The ability to accomplish this objective is based on the computational scheme developed by Radian Corporation during APCO Contract 22-69-138. Using this equilibrium subroutine, SO_2 (and CO_2) partial pressures above a given scrubber liquor can be calculated provided accurate chemical analyses are obtained. These calculated equilibrium partial pressures can then be compared to measured experimental partial pressures for the flue gas in contact with the liquor at the scrubber outlet. This comparison provides a quantitative index of vapor-liquid mass transfer capability. Appropriate test parameters can be varied to examine a range of scrubber performance.

3.0 EQUILIBRIUM CALCULATIONS

Copies of computer outputs for equilibrium calculations based on chemical analyses of appropriate scrubber liquors are

attached. Important aspects of the format for this output are described below and are indicated by numbered brackets on the first case.

For each of the Type I Runs, measured chemical species (aqueous) included equivalent concentrations of SO_2, CO_2, SO_3, N_2O_5, CaO, MgO, Na_2O, and HCl. These values are shown as inputs to each equilibrium calculation [1]. The scrubber liquor temperature is also input to the program [2]. Equilibrium concentrations, activities, and activity coefficients for all important species are calculated by the routine and printed as output [3]. The equilibrium partial pressures of CO_2 and SO_2 above a liquor of the composition given by the input species are also calculated and printed [4]. Finally, the pH and ionic strength [5] are calculated and printed.

The calculated value of pH is derived from the electroneutrality constraint for the liquor. Thus, it provides an important indication of the accuracy of the input species analyses. If one or more cation analyses are high, for example, electroneutrality would require that the calculated value of pH be higher. If anion analyses were high, the calculated pH would be lower than the actual pH.

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2

INPUT MOLES

APCO INHOUSE EXPERIMENTS - TYPE I, NO. 1

SO2	=5.00000-03						
CO2	=3.98000-04						
SO3	=1.93000-03	N2O5	=1.07000-04	CAO	=1.31000-03	MGO	=6.96000-04
NA2O	=6.18000-04	HCL	=1.49000-03	H2O	=5.55062+01		

1

AQUEOUS SOLUTION EQUILIBRIA

3

COMPONENT	MOLALITY	ACTIVITY	ACTIVITY COEFFICIENT
H2O			9.997-01
H+	3.818-03	3.451-03	9.039-01
OH-	6.054-12	5.408-12	8.933-01
HSO3-	3.895-03	3.484-03	8.944-01
SO3--	8.592-08	5.498-08	6.399-01
SO4--	1.319-03	8.257-04	6.261-01
HCO3-	6.267-08	5.605-08	8.944-01
CO3--	1.385-15	8.861-16	6.399-01
NO3-	2.135-04	1.887-04	8.836-01
HSO4-	3.939-04	3.519-04	8.933-01
H2SO3	1.105-03	1.108-03	1.002+00
H2CO3	3.980-04	3.988-04	1.002+00
CA++	1.170-03	7.528-04	6.435-01
CAOH+	1.143-13	1.021-13	8.933-01
CASO3	1.148-07	1.150-07	1.002+00
CACO3	1.168-15	1.170-15	1.002+00
CAHCO3+	9.149-10	8.173-10	8.933-01
CASO4	1.397-04	1.400-04	1.002+00
CANO3+	4.258-07	3.804-07	8.933-01
MG++	6.239-04	3.973-04	6.368-01
MGOH+	1.031-12	9.211-13	8.933-01
MGSO3	1.990-08	1.994-08	1.002+00
MGHCO3+	2.380-10	2.126-10	8.933-01
MGSO4	7.217-05	7.232-05	1.002+00
MGCO3	9.764-16	9.784-16	1.002+00
NA+	1.230-03	1.104-03	8.972-01
NAOH	1.603-15	1.607-15	1.002+00
NACO3-	2.161-17	1.930-17	8.933-01
NAHCO3	3.472-11	3.479-11	1.002+00
NASO4-	5.642-06	5.040-06	8.933-01

NANO3	8.273-08	8.290-08	1.002+00
CL-	1.490-03	1.330-03	8.928-01

4
PSO2 =1.21478-03 ATM.
PCO2 =1.44268-02 ATM.

MOLECULAR WATER = 9.99913-01 KGS.

PH = 2.462 IONIC STRENGTH = 1.17484-02

RES. E.N. = -1.733-10

5

77

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INPUT MOLES

APCO INHOUSE EXPERIMENTS - TYPE I, NO. 1A

SO2	=4.76000-03						
CO2	=3.98000-04						
SO3	=2.39000-03	N2O5	=1.07000-04	CAO	=1.50000-03	MGO	=5.02000-04
NA2O	=7.80000-04	HCL	=1.80000-03	H2O	=5.55062+01		

AQUEOUS SOLUTION EQUILIBRIA

COMPONENT	MOLALITY	ACTIVITY	ACTIVITY COEFFICIENT
H2O			9.997-01
H+	4.310-03	3.884-03	9.011-01
OH-	5.400-12	4.805-12	8.898-01
HSO3-	3.612-03	3.217-03	8.909-01
SO3--	7.163-08	4.512-08	6.299-01
SO4--	1.604-03	9.874-04	6.154-01
HCO3-	5.591-08	4.981-08	8.909-01
CO3--	1.111-15	6.997-16	6.299-01
NO3-	2.134-04	1.877-04	8.793-01
HSO4-	5.322-04	4.735-04	8.898-01
H2SO3	1.149-03	1.151-03	1.002+00
H2CO3	3.980-04	3.989-04	1.002+00
CA++	1.315-03	8.331-04	6.337-01
CAOH+	1.128-13	1.004-13	8.898-01
CASO3	1.042-07	1.045-07	1.002+00
CACO3	1.020-15	1.022-15	1.002+00
CAHCO3+	9.035-10	8.039-10	8.898-01
CASO4	1.849-04	1.853-04	1.002+00
CANO3+	4.707-07	4.188-07	8.898-01
MG++	4.419-04	2.769-04	6.267-01
MGOH+	6.412-13	5.705-13	8.898-01
MGSO3	1.138-08	1.140-08	1.002+00
MGHCO3+	1.481-10	1.317-10	8.898-01
MGSO4	6.015-05	6.028-05	1.002+00
MGCO3	5.374-16	5.386-16	1.002+00
NA+	1.552-03	1.387-03	8.938-01
NAOH	1.789-15	1.793-15	1.002+00
NACO3-	2.152-17	1.915-17	8.898-01
NAHCO3	3.876-11	3.885-11	1.002+00
NASO4-	8.510-06	7.571-06	8.898-01

NANO3	1.034-07	1.036-07	1.002+00
CL-	1.800-03	1.601-03	8.892-01

PSO2 =1.26274-03 ATM.
PCO2 =1.44299-02 ATM.

MOLECULAR WATER = 9.99912-01 KGS.

PH = 2.411 IONIC STRENGTH = 1.27363-02 RES. E.N. = -2.866-08

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INPUT MOLES

SO2 =4.70000-03
CO2 =2.51000-03
SO3 =1.27000-03 N2O5 =1.32000-04 CAO =1.28000-03 MGO =5.14000-04
NA2O =6.56000-04 HCL =1.59000-03 H2O =5.55062+01

APCO INHOUSE EXPERIMENTS - TYPE I - NO. 2

AQUEOUS SOLUTION EQUILIBRIA

COMPONENT	MOLALITY	ACTIVITY	ACTIVITY COEFFICIENT
H2O			9.997-01
H+	3.096-03	2.804-03	9.085-01
OH-	7.402-12	6.655-12	8.991-01
HSO3-	3.815-03	3.434-03	9.001-01
SO3--	1.016-07	6.669-08	6.564-01
SO4--	9.014-04	5.804-04	6.439-01
HCO3-	4.832-07	4.349-07	9.001-01
CO3--	1.289-14	8.461-15	6.564-01
NO3-	2.634-04	2.345-04	8.905-01
HSO4-	2.235-04	2.010-04	8.991-01
H2SO3	8.855-04	8.870-04	1.002+00
H2CO3	2.510-03	2.514-03	1.002+00
CA++	1.178-03	7.771-04	6.596-01
CAOH+	1.442-13	1.297-13	8.991-01
CASO3	1.438-07	1.440-07	1.002+00
CACO3	1.151-14	1.153-14	1.002+00
CAHCO3+	7.281-09	6.546-09	8.991-01
CASO4	1.014-04	1.016-04	1.002+00
CANO3+	5.429-07	4.882-07	8.991-01
MG++	4.744-04	3.100-04	6.535-01
MGOH+	9.639-13	8.666-13	8.991-01
MGSO3	1.894-08	1.387-08	1.002+00
MGHCO3+	1.432-09	1.288-09	8.991-01
MGSO4	3.960-05	3.967-05	1.002+00
MGCO3	7.278-15	7.291-15	1.002+00
NA+	1.308-03	1.180-03	9.026-01
NAOH	2.111-15	2.114-15	1.002+00
NACO3-	2.192-16	1.971-16	8.991-01
NAHCO3	2.892-10	2.897-10	1.002+00
NASO4-	4.214-06	3.788-06	8.991-01

NANO3		1.100-07	1.102-07	1.002+00
CL-		1.590-03	1.429-03	8.987-01

PSO2 =9.72981-04 ATM.
PCO2 =9.03596-02 ATM.

TYPE I - NO. 2

MOLECULAR WATER = 9.99889-01 KGS.

PH = 2.552 IONIC STRENGTH = 1.02535-02 RES. E.N. = -2.849-09

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INPUT MOLES

APCO INHOUSE EXPERIMENTS - TYPE I, NO. 3

SO2	=4.60000-03						
CO2	=2.55000-03						
SO3	=1.69000-03	N2O5	=1.25000-04	CAO	=1.26000-03	MGO	=4.60000-04
NA2O	=6.42000-04	HCL	=1.60000-03	H2O	=5.55062+01		

AQUEOUS SOLUTION EQUILIBRIA

COMPONENT	MOLALITY	ACTIVITY	ACTIVITY COEFFICIENT
H2O			8.997-01
H+	3.751-03	3.400-03	9.066-01
OH-	6.120-12	5.488-12	8.967-01
HSO3-	3.592-03	3.225-03	8.977-01
SO3--	7.951-08	5.165-08	6.496-01
SO4--	1.159-03	7.439-04	6.366-01
HCO3-	4.059-07	3.644-07	8.977-01
CO3--	9.000-15	5.846-15	6.496-01
NO3-	2.494-04	2.214-04	8.877-01
HSO4-	3.483-04	3.123-04	8.967-01
H2SO3	1.008-03	1.010-03	1.002+00
H2CO3	2.550-03	2.555-03	1.002+00
CA++	1.136-03	7.414-04	6.529-01
CAOH+	1.138-13	1.020-13	8.967-01
CASO3	1.062-07	1.064-07	1.002+00
CACO3	7.588-15	7.603-15	1.002+00
CAHCO3+	5.836-09	5.233-09	8.967-01
CASO4	1.240-04	1.242-04	1.002+00
CANO3+	4.904-07	4.397-07	8.967-01
MG++	4.160-04	2.690-04	6.465-01
MGOH+	7.058-13	6.329-13	8.967-01
MGSO3	1.266-08	1.268-08	1.002+00
MGHCO3+	1.044-09	9.360-10	8.967-01
MGSO4	4.403-05	4.411-05	1.002+00
MGCO3	4.362-15	4.370-15	1.002+00
NA+	1.279-03	1.151-03	9.003-01
NAOH	1.597-15	1.701-15	1.002+00
NACO3-	1.481-16	1.328-16	8.967-01
NAHCO3	2.355-10	2.359-10	1.002+00
NASO4-	5.291-06	4.736-06	8.967-01

NANO3	1.313-07	1.015-07	1.002+00
CL-	1.600-03	1.434-03	8.963-01

PSO2 =1.10812-03 ATM.
PCO2 =9.24241-02 ATM.

MOLECULAR WATER = 9.99881-01 KGS.

PH = 2.468 IONIC STRENGTH = 1.08532-02 RES. E.N. = -3.531-11

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INPUT MOLES

APCO INHOUSE EXPERIMENTS - TYPE I, NO. 3A

SO2	=4.58000-03						
CO2	=3.75000-04						
SO3	=1.42000-03	N2O5	=1.47000-04	CAO	=1.41000-03	MGO	=5.10000-04
NA2O	=7.80000-04	HCL	=1.90000-03	H2O	=5.55062+01		

AQUEOUS SOLUTION EQUILIBRIA

COMPONENT	MOLALITY	ACTIVITY	ACTIVITY COEFFICIENT
H2O			9.397-01
H+	3.104-03	2.813-03	9.064-01
OH-	7.399-12	6.632-12	8.964-01
HSO3-	3.717-03	3.336-03	8.974-01
SO3--	9.954-08	6.457-08	6.487-01
SO4--	1.004-03	6.383-04	6.356-01
HCO3-	7.216-08	6.476-08	8.974-01
CO3--	1.936-15	1.256-15	6.487-01
NO3-	2.932-04	2.602-04	8.873-01
HSO4-	2.474-04	2.218-04	8.964-01
H2SO3	8.630-04	8.647-04	1.002+00
H2CO3	3.750-04	3.757-04	1.002+00
CA++	1.289-03	8.403-04	6.521-01
CAOH+	1.559-13	1.398-13	8.964-01
CASO3	1.505-07	1.508-07	1.002+00
CACO3	1.847-15	1.851-15	1.002+00
CAHCO3+	1.176-09	1.054-09	8.964-01
CASO4	1.206-04	1.208-04	1.002+00
CANO3+	6.533-07	5.856-07	8.964-01
MG++	4.676-04	3.019-04	6.457-01
MGOH+	9.578-13	8.586-13	8.964-01
MGSO3	1.776-08	1.779-08	1.002+00
MGHCO3+	2.083-10	1.867-10	8.964-01
MGSO4	4.240-05	4.249-05	1.002+00
MGCO3	1.052-15	1.054-15	1.002+00
NA+	1.554-03	1.399-03	9.000-01
NAOH	2.493-15	2.498-15	1.002+00
NACO3-	3.868-17	3.467-17	8.964-01
NAHCO3	5.095-11	5.095-11	1.002+00
NASO4-	5.509-06	4.938-06	8.964-01

NANO3	1.446-07	1.449-07	1.002+00
CL-	1.900-03	1.702-03	8.960-01

PSO2 =9.48432-04 ATM.
PCO2 =1.35903-02 ATM.

MOLECULAR WATER = 9.99931-01 KGS.

PH = 2.551 IONIC STRENGTH = 1.09326-02 RES. E.N. = -9.442-09

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INPUT MOLES

APCO INHOUSE EXPERIMENTS - TYPE I, NO. 3B

SO2	=8.04000-03						
CO2	=2.83000-04						
SO3	=3.59000-03	N2O5	=1.07000-04	CAO	=1.36000-03	MGO	=3.40000-04
NA2O	=1.56000-03	HCL	=1.00000-03	H2O	=5.55062+01		

AQUEOUS SOLUTION EQUILIBRIA

COMPONENT	MOLALITY	ACTIVITY	ACTIVITY COEFFICIENT
H2O			9.996-01
H+	6.523-03	5.825-03	8.930-01
OH-	2.647-12	2.327-12	8.793-01
HSO3-	5.626-03	4.953-03	8.804-01
SO3--	8.265-08	4.967-08	6.009-01
SO4--	2.340-03	1.366-03	5.840-01
HCO3-	2.577-08	2.269-08	8.804-01
CO3--	3.272-16	1.966-16	6.009-01
NO3-	2.135-04	1.849-04	8.663-01
HSO4-	9.777-04	8.597-04	8.793-01
H2SO3	2.415-03	2.422-03	1.003+00
H2CO3	2.830-04	2.838-04	1.003+00
CA++	1.156-03	7.002-04	6.056-01
CAOH+	4.509-14	3.965-14	8.793-01
CASO3	9.115-08	9.141-08	1.003+00
CACO3	2.285-16	2.291-16	1.003+00
CAHCO3+	3.385-10	2.976-10	8.793-01
CASO4	2.036-04	2.042-04	1.003+00
CANO3+	3.438-07	3.023-07	8.793-01
MG++	2.932-04	1.753-04	5.977-01
MGOH+	1.878-13	1.652-13	8.793-01
MGSO3	7.553-09	7.574-09	1.003+00
MGHCO3+	4.208-11	3.700-11	8.793-01
MGSO4	4.683-05	4.697-05	1.003+00
MGCO3	9.034-17	9.060-17	1.003+00
NA+	3.097-03	2.738-03	8.841-01
NAOH	1.710-15	1.715-15	1.003+00
NACO3-	1.169-17	1.028-17	8.793-01
NAHCO3	3.484-11	3.494-11	1.003+00
NASO4-	2.291-05	2.014-05	8.793-01

NANO3	2.010-07	2.016-07	1.003+00
CL-	1.000-03	8.786-04	8.784-01

PSO2 =2.28385-03 ATM.
PCO2 =9.18043-03 ATM.

MOLECULAR WATER = 9.99842-01 KGS.

PH = 2.235 IONIC STRENGTH = 1.63085-02 RES. E.N. = -2.510-09

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INPUT MOLES

APCO INHOUSE EXPERIMENTS - TYPE I, NO. 4

SO2	=4.00000-03						
CO2	=1.43000-03						
SO3	=1.57000-03	N2O5	=1.43000-04	CAO	=1.34000-03	MGO	=4.43000-04
NA2O	=6.73000-04	HCL	=2.04000-03	H2O	=5.55052+01		

AQUEOUS SOLUTION EQUILIBRIA

COMPONENT	MOLALITY	ACTIVITY	ACTIVITY COEFFICIENT
H2O			9.997-01
H+	3.435-03	3.116-03	9.070-01
OH-	6.675-12	5.989-12	8.972-01
HSO3-	3.131-03	2.858-03	8.982-01
SO3--	7.672-08	4.394-08	5.510-01
SO4--	1.099-03	7.011-04	6.381-01
HCO3-	2.482-07	2.230-07	8.982-01
CO3--	5.997-15	3.904-15	6.510-01
NO3-	2.853-04	2.534-04	8.883-01
HSO4-	3.007-04	2.698-04	8.972-01
H2SO3	8.198-04	8.203-04	1.002+00
H2CO3	1.430-03	1.433-03	1.002+00
CA++	1.214-03	7.945-04	6.543-01
CAOH+	1.330-13	1.193-13	8.972-01
CASO3	1.101-07	1.103-07	1.002+00
CACO3	5.430-15	5.440-15	1.002+00
CAHCO3+	3.825-09	3.431-09	8.972-01
CASO4	1.252-04	1.255-04	1.002+00
CANO3+	6.010-07	5.393-07	8.972-01
MG++	4.028-04	2.610-04	6.480-01
MGOH+	7.469-13	6.701-13	8.972-01
MGSO3	1.188-08	1.190-08	1.002+00
MGHCO3+	6.194-10	5.557-10	8.972-01
MGSO4	4.028-05	4.034-05	1.002+00
MGCO3	2.827-15	2.832-15	1.002+00
NA+	1.341-03	1.208-03	9.008-01
NAOH	1.943-15	1.947-15	1.002+00
NACO3-	1.037-16	9.305-17	8.972-01
NAHCO3	1.512-10	1.514-10	1.002+00
NASO4-	5.219-06	4.682-06	8.972-01

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NANO3	1.216-07	1.219-07	1.002+00
CL-	2.040-03	1.830-03	8.968-01

PSO2 =8.99802-04 ATM.
PCO2 =5.18249-02 ATM.

MOLECULAR WATER = 9.99916-01 KGS.

PH = 2.506 IONIC STRENGTH = 1.07264-02 RES. E.N. = -1.307-09

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INPUT MOLES

APCO INHOUSE EXPERIMENTS - TYPE I, NO. 5

SO2	=2.54000-03						
CO2	=1.55000-03						
SO3	=4.10000-03	N2O5	=1.07000-04	CAO	=1.32000-03	MGO	=4.40000-04
NA2O	=6.93000-04	HCL	=2.05000-03	H2O	=5.55062+01		

AQUEOUS SOLUTION EQUILIBRIA

COMPONENT	MOLALITY	ACTIVITY	ACTIVITY COEFFICIENT
H2O			9.997-01
H+	6.126-03	5.492-03	8.966-01
OH-	3.843-12	3.397-12	8.841-01
HSO3-	1.756-03	1.554-03	8.852-01
SO3--	2.510-09	1.541-08	6.141-01
SO4--	2.590-03	1.550-03	5.983-01
HCO3-	1.550-07	1.372-07	8.852-01
CO3--	2.219-15	1.363-15	6.141-01
NO3-	2.136-04	1.863-04	8.723-01
HSO4-	1.189-03	1.051-03	8.841-01
H2SO3	7.845-04	7.865-04	1.003+00
H2CO3	1.550-03	1.554-03	1.003+00
CA++	1.086-03	5.715-04	6.183-01
CAOH+	6.470-14	5.720-14	8.841-01
CASO3	2.869-08	2.876-08	1.003+00
CACO3	1.601-15	1.605-15	1.003+00
CAHCO3+	2.019-09	1.785-09	8.841-01
CASO4	2.338-04	2.344-04	1.003+00
CANO3+	3.790-07	3.350-07	8.841-01
MG++	3.642-04	2.225-04	6.108-01
MGOH+	3.666-13	3.241-13	8.841-01
MGSO3	3.122-09	3.129-09	1.003+00
MGHCO3+	3.298-10	2.915-10	8.841-01
MGSO4	7.582-05	7.601-05	1.003+00
MGCO3	8.407-16	8.428-16	1.003+00
NA+	1.374-03	1.221-03	8.885-01
NAOH	1.114-15	1.117-15	1.003+00
NACO3-	3.715-17	3.284-17	8.841-01
NAHCO3	9.398-11	9.422-11	1.003+00
NASO4-	1.184-05	1.046-05	8.841-01

NANO3	9.033-08	9.056-08	1.003+00
CL-	2.050-03	1.811-03	8.834-01

PSO2 =8.62702-04 ATM.
PCO2 =5.62191-02 ATM.

MOLECULAR WATER = 9.99895-01 KGS.

PH = 2.260 IONIC STRENGTH = 1.44410-02 RES. E.N. = -2.326-08

27 JAN 71 11:35:46.517 TEMPERATURE 33.330 DEG. C

INPUT MOLES

APCO INHOUSE EXPERIMENTS - TYPE I, NO. 6

SO2	=1.88000-02						
CO2	=1.09000-03						
SO3	=3.00000-03	N2O5	=1.25000-04	CAO	=1.38000-03	MGO	=4.73000-04
NA2O	=1.46000-02	HCL	=1.90000-03	H2O	=5.55062+01		

AQUEOUS SOLUTION EQUILIBRIA

COMPONENT	MOLALITY	ACTIVITY	ACTIVITY COEFFICIENT
H2O			9.991-01
H+	3.617-07	3.115-07	8.612-01
OH-	7.174-08	5.988-08	8.345-01
HSO3-	1.356-02	1.133-02	8.354-01
SO3--	4.067-03	1.980-03	4.870-01
SO4--	2.717-03	1.249-03	4.595-01
HCO3-	7.036-04	5.877-04	8.354-01
CO3--	2.114-07	1.029-07	4.870-01
NO3-	2.480-04	2.001-04	8.070-01
HSO4-	5.756-08	4.803-08	8.345-01
H2SO3	3.230-07	3.251-07	1.007+00
H2CO3	3.750-04	3.775-04	1.007+00
CA++	3.579-04	1.774-04	4.958-01
CAOH+	3.192-10	2.663-10	8.345-01
CASO3	9.702-04	9.766-04	1.007+00
CACO3	3.192-08	3.203-08	1.007+00
CAHCO3+	2.420-06	2.020-06	8.345-01
CASO4	4.957-05	4.990-05	1.007+00
CANO3+	1.140-07	9.510-08	8.345-01
MG++	2.357-04	1.143-04	4.850-01
MGOH+	3.516-09	2.934-09	8.345-01
MGSO3	2.053-04	2.066-04	1.007+00
MGHCO3+	7.639-07	6.416-07	8.345-01
MGSO4	3.126-05	3.147-05	1.007+00
MGCO3	3.249-08	3.270-08	1.007+00
NA+	2.899-02	2.443-02	8.428-01
NAOH	3.911-10	3.937-10	1.007+00
NACO3-	5.947-08	4.963-08	8.345-01
NAHCO3	8.023-06	8.076-06	1.007+00
NASO4-	2.022-04	1.687-04	8.345-01

NANO3	1.934-06	1.947-06	1.007+00
CL-	1.900-03	1.580-03	8.315-01

PSO2 =3.56814-07 ATM.
PCO2 =1.36651-02 ATM.

MOLECULAR WATER = 9.99882-01 KGS.

PH = 6.507 IONIC STRENGTH = 3.75598-02 RES. E.N. = 2.071-10

21 DEC 70 11:23:44.884 TEMPERATURE 30.000 DEG. C

INPUT MOLES

APCO INHOUSE EXPERIMENTS - TYPE I, NO. 6A

SO2	=2.15000-02						
CO2	=1.09000-03						
SO3	=5.30000-03	N2O5	=1.15000-04	CAO	=8.90000-04	MGO	=3.20000-04
NA2O	=2.12000-02	HCL	=1.15000-03	H2O	=5.55062+01		

AQUEOUS SOLUTION EQUILIBRIA

COMPONENT	MOLALITY	ACTIVITY	ACTIVITY COEFFICIENT
H2O			9.988-01
H+	1.472-07	1.248-07	8.474-01
OH-	1.452-07	1.178-07	8.112-01
HSO3-	1.106-02	8.972-03	8.109-01
SO3--	9.542-03	4.126-03	4.324-01
SO4--	4.812-03	1.920-03	3.991-01
HCO3-	8.854-04	7.180-04	8.109-01
CO3--	6.857-07	2.965-07	4.324-01
NO3-	2.276-04	1.757-04	7.719
HSO4-	3.299-08	2.676-08	8.112-
H2SO3	9.524-08	9.620-08	1.010+00
H2CO3	1.884-04	1.903-04	1.010+00
CA++	1.476-04	6.559-05	4.443-01
CAOH+	2.335-10	1.894-10	8.112-01
CASO3	7.143-04	7.215-04	1.010+00
CACO3	3.247-08	3.280-08	1.010+00
CAHCO3+	1.097-06	8.898-07	8.112-01
CASO4	2.697-05	2.724-05	1.010+00
CANO3+	3.434-08	2.785-08	8.112-01
MG++	1.173-04	5.079-05	4.329-01
MGOH+	3.029-09	2.457-09	8.112-01
MGSO3	1.827-04	1.846-04	1.010+00
MGHCO3+	4.211-07	3.416-07	8.112-01
MGSO4	1.951-05	1.971-05	1.010+00
MGCO3	3.975-08	4.015-08	1.010+00
NA+	4.195-02	3.445-02	8.213-01
NAOH	1.081-09	1.092-09	1.010+00
NACO3-	2.424-07	1.966-07	8.112-01
NAHCO3	1.377-05	1.391-05	1.010+00
NASO4-	4.421-04	3.586-04	8.112-01

NANO3	2.386-06	2.410-06	1.010+00
CL-	1.150-03	9.268-04	8.058-01

PSO2 =9.43203-08 ATM.
PCO2 =6.33582-03 ATM.

MOLECULAR WATER = 9.99899-01 KGS.

PH = 6.904 IONIC STRENGTH = 5.70966-02 RES. E.N. = 2.020-09

APCO INHOUSE EXPERIMENTS - TYPE I, NO. 7

07 DEC 70 08:22:39.295 TEMPERATURE 35.000 DEG. C

INPUT MOLES

SO2	=2.17000-02						
CO2	=5.20000-04						
SO3	=1.59000-03	N2O5	=1.86000-04	CAO	=1.67000-03	MGO	=5.43000-04
NA2O	=1.88000-02	HCL	=1.95000-03	H2O	=5.55062+01		

AQUEOUS SOLUTION EQUILIBRIA

COMPONENT	MOLALITY	ACTIVITY	ACTIVITY COEFFICIENT
H2O			9.990-01
H+	6.787-08	5.762-08	8.489-01
OH-	4.464-07	3.638-07	8.145-01
HSO3-	7.354-03	5.991-03	8.146-01
SO3--	1.253-02	5.518-03	4.404-01
SO4--	1.443-03	5.890-04	4.081-01
HCO3-	4.668-04	3.803-04	8.146-01
CO3--	8.397-07	3.698-07	4.404-01
NO3-	3.894-04	3.865-04	7.777-01
HSO4-	5.412-09	4.408-09	8.145-01
H2SO3	3.251-08	3.291-08	1.009+00
H2CO3	4.421-05	4.461-05	1.009+00
CA++	2.069-04	9.345-05	4.516-01
CAOH+	1.058-09	8.615-10	8.145-01
CASO3	1.450-03	1.463-03	1.009+00
CACO3	6.123-08	6.180-08	1.009+00
CAHCO3+	8.556-07	6.969-07	8.145-01
CASO4	1.255-05	1.266-05	1.009+00
CANO3+	9.262-08	7.545-08	8.145-01
MG++	1.647-04	7.249-05	4.402-01
MGOH+	1.417-08	1.154-08	8.145-01
MGSO3	3.682-04	3.716-04	1.009+00
MGHCO3+	3.263-07	2.658-07	8.145-01
MGSO4	9.737-05	9.827-06	1.009+00
MGCO3	7.536-08	7.606-08	1.009+00
NA+	3.747-02	3.089-02	8.244-01
NAOH	2.995-09	3.0[illegible]-09	1.009+00
NACO3-	2.802-07	2.282-07	8.145-01
NAHCO3	6.545-06	6.606-06	1.009+00
NASO4-	1.247-04	1.016-04	8.145-01

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NANO3	3.491-06	3.523-06	1.009+00
CL-	1.950-03	1.579-03	8.098-01

PSO2 =3.81986-08 ATM.
PCO2 =1.68341-03 ATM.

MOLECULAR WATER = 9.99946-01 KGS.

PH = '.239 IONIC STRENGTH = 5.25568-02 RES. E.N. = 1.114-09

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APCO INHOUSE EXPERIMENTS - TYPE I, NO. 8

07 DEC 70 08:22:24.429 TEMPERATURE 33.330 DEG. C

INPUT MOLES

SO2	=2.27000-02						
CO2	=5.00000-04						
SO3	=5.40000-03	N2O5	=1.86000-04	CAO	=1.50000-03	MGO	=7.16000-04
NA2O	=1.92000-02	HCL	=2.25000-03	H2O	=5.55062+01		

AQUEOUS SOLUTION EQUILIBRIA

COMPONENT	MOLALITY	ACTIVITY	ACTIVITY COEFFICIENT
H2O			9.988-01
H+	3.795-07	3.230-07	8.511-01
OH-	7.057-08	5.773-08	8.180-01
HSO3-	1.632-02	1.335-02	8.183-01
SO3--	5.022-03	2.252-03	4.483-01
SO4--	4.830-03	2.013-03	4.168-01
HCO3-	3.206-04	2.623-04	8.183-01
CO3--	9.884-08	4.431-08	4.483-01
NO3-	3.683-04	2.883-04	7.829-01
HSO4-	9.815-08	8.029-08	8.180-01
H2SO3	3.938-07	3.973-07	1.009+00
H2CO3	1.732-04	1.747-04	1.009+00
CA++	3.697-04	1.697-04	4.592-01
CAOH+	3.004-10	2.457-10	8.180-01
CASO3	1.053-03	1.062-03	1.009+00
CACO3	1.308-08	1.319-08	1.009+00
CAHCO3+	1.054-06	8.626-07	8.180-01
CASO4	7.630-05	7.697-05	1.009+00
CANO3+	1.602-07	1.311-07	8.180-01
MG++	3.393-04	1.519-04	4.478-01
MGOH+	4.597-09	3.760-09	8.180-01
MGSO3	3.095-04	3.122-04	1.009+00
MGHCO3+	4.653-07	3.806-07	8.180-01
MGSO4	6.684-05	6.743-05	1.009+00
MGCO3	1.855-08	1.871-08	1.009+00
NA+	3.797-02	3.142-02	8.276-01
NAOH	4.840-10	4.8[illegible]-10	1.009+00
NACO3-	3.360-08	2.748-08	8.180-01
NAHCO3	4.595-06	4.636-06	1.009+00
NASO4-	4.276-04	3.498-04	8.180-01

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NANO3	3.576-06	3.607-06	1.009+00
CL-	2.250-03	1.831-03	8.136-01

PSO2 =4.36168-07 ATM.
PCO2 =6.32547-03 ATM.

MOLECULAR WATER = 9.99867-01 KGS.

PH = 6.491 TONIC STRENGTH = 4.99505-02 RES. E.N. = 1.396-09

21 DEC 70 11:23:57.740 TEMPERATURE 34.440 DEG. C

INPUT MOLES

APCO INHOUSE EXPERIMENTS - TYPE I, NO. 8A

SO2	=2.63000-02						
CO2	=9.43000-04						
SO3	=3.10000-03	N2O5	=1.07000-04	CAO	=1.06000-03	MGO	=3.30000-04
NA2O	=1.78000-02	HCL	=1.20000-03	H2O	=5.55062+01		

AQUEOUS SOLUTION EQUILIBRIA

COMPONENT	MOLALITY	ACTIVITY	ACTIVITY COEFFICIENT
H2O			9.989-01
H+	7.652-07	6.551-07	8.561-01
OH-	3.721-08	3.076-08	8.265-01
HSO3-	2.229-02	1.844-02	8.272-01
SO3--	3.218-03	1.506-03	4.681-01
SO4--	2.789-03	1.224-03	4.387-01
HCO3-	4.454-04	3.685-04	8.272-01
CO3--	6.672-08	3.123-08	4.681-01
NO3-	2.120-04	1.687-04	7.956-01
HSO4-	1.239-07	1.024-07	8.265-01
H2SO3	1.130-06	1.139-06	1.008+00
H2CO3	4.898-04	4.935-04	1.008+00
CA++	3.366-04	1.608-04	4.778-01
CAOH+	1.512-10	1.250-10	8.265-01
CASO3	6.775-04	6.827-04	1.008+00
CACO3	8.858-09	8.925-09	1.008+00
CAHCO3+	1.400-06	1.157-06	8.265-01
CASO4	4.461-05	4.494-05	1.008+00
CANO3+	9.091-08	7.514-08	8.265-01
MG++	1.859-04	8.678-05	4.667-01
MGOH+	1.404-09	1.161-09	8.265-01
MGSO3	1.198-04	1.207-04	1.008+00
MGHCO3+	3.718-07	3.073-07	8.265-01
MGSO4	2.391-05	2.409-05	1.008+00
MGCO3	7.580-09	7.638-09	1.008+00
NA+	3.536-02	2.954-02	8.355-01
NAOH	2.427-10	2.445-10	1.008+00
NACO3-	2.221-08	1.836-08	8.265-01
NAHCO3	6.074-06	6.120-06	1.008+00
NASO4-	2.434-04	2.011-04	8.265-01

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NANO3	1.968-06	1.983-06	1.008+00
CL-	1.200-03	9.877-04	8.229-01

PSO2 =1.29719-06 ATM.
PCO2 =1.83666-02 ATM.

MOLECULAR WATER = 9.99797-01 KGS.

PH = 6.184 IONIC STRENGTH = 4.29329-02 RES. E.N. = 4.179-10

07 DEC 70 08:22:49.222

APCO INHOUSE EXPERIMENTS - TYPE I, NO. 9

TEMPERATURE 31.660 DEG. C

INPUT MOLES

SO2	=2.04000-02						
CO2	=6.73000-04						
SO3	=5.60000-03	N2O5	=1.07000-04	CAO	=1.51000-03	MGO	=5.84000-04
NA2O	=2.01000-02	HCL	=2.25000-03	H2O	=5.55062+01		

AQUEOUS SOLUTION EQUILIBRIA

COMPONENT	MOLALITY	ACTIVITY	ACTIVITY COEFFICIENT
H2O			9.989-01
H+	1.573-07	1.335-07	8.485-01
OH-	1.525-07	1.241-07	8.133-01
HSO3-	1.063-02	8.644-03	8.133-01
SO3--	8.272-07	3.619-03	4.375-01
SO4--	5.054-03	2.046-03	4.048-01
HCO3-	5.410-04	4.400-04	8.133-01
CO3--	3.996-07	1.748-07	4.375-01
NO3-	2.118-04	1.643-04	7.755-01
HSO4-	3.942-08	3.206-08	8.133-01
H2SO3	1.017-07	1.027-07	1.010+00
H2CO3	1.217-04	1.228-04	1.010+00
CA++	2.703-04	1.214-04	4.490-01
CAOH+	4.589-10	3.733-10	8.133-01
CASO3	1.184-03	1.196-03	1.010+00
CACO3	3.614-08	3.649-08	1.010+00
CAHCO3+	1.256-06	1.021-06	8.133-01
CASO4	5.425-05	5.477-05	1.010+00
CANO3+	6.237-08	5.073-08	8.133-01
MG++	2.250-04	9.845-05	4.376-01
MGOH+	6.302-09	5.126-09	8.133-01
MGSO3	3.164-04	3.195-04	1.010+00
MGHCO3+	5.037-07	4.097-07	8.133-01
MGSO4	4.210-05	4.250-05	1.010+00
MGCO3	4.641-08	4.685-08	1.010+00
NA+	3.974-02	3.272-02	8.233-01
NAOH	1.082-09	1.0 -09	1.010+00
NACO3-	1.371-07	1.116-07	8.133-01
NAHCO3	8.019-06	8.096-06	1.010+00
NASO4-	4.505-04	3.664-04	8.133-01

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NANO3	2.120-06	2.140-06	1.010+00
CL-	2.250-03	1.819-03	8.083-01

PS02 =1.06560-07 ATM.
PC02 =4.26551-03 ATM.

MOLECULAR WATER = 9.99917-01 KGS.

PH = 6.874 IONIC STRENGTH = 5.45567-02 RES. E.N. = 6.369-09

27 JAN 71 11:36:02.144 TEMPERATURE 25.230 DEG. C

INPUT MOLES

APCO INHOUSE EXPERIMENTS - TYPE I, NO. 9A

SO2	=2.31000-02						
CO2	=8.56000-04						
SO3	=1.03000-03	N2O5	=9.00000-05	CAO	=1.06000-03	MGO	=3.70000-04
NA2O	=1.42000-02	HCL	=1.10000-03	H2O	=5.55062+01		

AQUEOUS SOLUTION EQUILIBRIA

COMPONENT	MOLALITY	ACTIVITY	ACTIVITY COEFFICIENT
H2O			9.991-01
H+	6.358-07	5.507-07	8.662-01
OH-	2.222-08	1.870-08	8.416-01
HSO3-	1.871-02	1.576-02	8.425-01
SO3--	3.520-03	1.774-03	5.038-01
SO4--	9.394-04	4.488-04	4.778-01
HCO3-	4.179-04	3.521-04	8.425-01
CO3--	5.969-08	3.008-08	5.038-01
NO3-	1.796-04	1.458-04	8.165-01
HSO4-	2.844-08	2.394-08	8.416-01
H2SO3	6.592-07	6.732-07	1.006+00
H2CO3	4.317-04	4.343-04	1.006+00
CA++	3.199-04	1.638-04	5.121-01
CAOH+	8.634-11	7.266-11	8.416-01
CASO3	7.240-04	7.284-04	1.006+00
CACO3	7.795-09	7.842-09	1.006+00
CAHCO3+	1.248-06	1.050-06	8.416-01
CASO4	1.496-05	1.505-05	1.006+00
CANO3+	5.896-08	4.962-08	8.416-01
MG++	2.078-04	1.042-04	5.016-01
MGOH+	8.937-10	7.521-10	8.416-01
MGSO3	1.536-04	1.545-04	1.006+00
MGHCO3+	3.970-07	3.341-07	8.416-01
MGSO4	8.263-06	8.313-06	1.006+00
MGCO3	7.814-09	7.861-09	1.006+00
NA+	2.833-02	2.406-02	8.493-01
NAOH	1.204-10	1.211-10	1.006+00
NACO3-	1.595-09	1.343-09	8.416-01
NAHCO3	4.736-06	4.764-06	1.006+00
NASO4-	6.756-05	5.685-05	8.416-01

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NANO3	1.388-06	1.397-06	1.006+00
CL-	1.100-03	9.230-04	8.390-01

PSO2 =5.58775-07 ATM.
PCO2 =1.27835-02 ATM.

MOLECULAR WATER = 9.99830-01 KGS.

PH = 6.259 IONIC STRENGTH = 3.43761-02 RES. E.N. = 1.941-10

27 JAN 71 11:35:56.453 TEMPERATURE 33.330 DEG. C

INPUT MOLES

APCO INHOUSE EXPERIMENTS - TYPE I, NO. 10

SO2	=1.13000-02						
CO2	=6.50000-04						
SO3	=4.00000-03	N2O5	=2.29000-04	CAO	=1.51000-03	MGO	=5.72000-04
NA2O	=9.81000-03	HCL	=2.25000-03	H2O	=5.55062+01		

AQUEOUS SOLUTION EQUILIBRIA

COMPONENT	MOLALITY	ACTIVITY	ACTIVITY COEFFICIENT
H2O			9.993-01
H+	1.101-06	9.607-07	8.729-01
OH-	2.279-08	1.941-08	8.519-01
HSO3-	9.767-03	8.332-03	8.531-01
SO3--	8.917-04	4.723-04	5.296-01
SO4--	3.552-03	1.799-03	5.064-01
HCO3-	2.407-04	2.054-04	8.531-01
CO3--	2.202-08	1.166-08	5.296-01
NO3-	4.550-04	3.782-04	8.311-01
HSO4-	2.505-07	2.134-07	8.519-01
H2SO3	7.340-07	7.375-07	1.005+00
H2CO3	4.049-04	4.068-04	1.005+00
CA++	7.863-04	4.219-04	5.366-01
CAOH+	2.411-10	2.054-10	8.519-01
CASO3	5.512-04	5.539-04	1.005+00
CACO3	8.589-09	8.630-09	1.005+00
CAHCO3+	1.970-06	1.679-06	8.519-01
CASO4	1.701-04	1.710-04	1.005+00
CANO3+	5.016-07	4.274-07	8.519-01
MG++	3.986-04	2.100-04	5.267-01
MGOH+	2.052-09	1.748-09	8.519-01
MGSO3	9.008-05	9.051-05	1.005+00
MGHCO3+	4.834-07	4.118-07	8.519-01
MGSO4	8.287-05	8.327-05	1.005+00
MGCO3	6.773-09	6.805-09	1.005+00
NA+	1.942-02	1.668-02	8.588-01
NAOH	8.675-11	8.717-11	1.005+00
NACO3-	4.506-09	3.839-09	8.519-01
NAHCO3	1.917-06	1.926-06	1.005+00
NASO4-	1.948-04	1.659-04	8.519-01

NANO3	2.499-06	2.511-06	1.005+00
CL-	2.250-03	1.913-03	8.500-01

PSO2 =8.09286-07 ATM.
PCO2 =1.47238-02 ATM.

MOLECULAR WATER = 9.99923-01 KGS.

PH = 6.017 IONIC STRENGTH = 2.74251-02 RES. E.N. = -1.712-10

21 DEC 70 11:24:09.378 TEMPERATURE 28.890 DEG. C

INPUT MOLES

APCO INHOUSE EXPERIMENTS - TYPE I, NO. 10A

SO2	=1.18000-02						
CO2	=2.93000-04						
SO3	=2.20000-03	N2O5	=1.40000-04	CAO	=1.43000-03	MGO	=4.00000-04
NA2O	=5.91000-03	HCL	=1.10000-03	H2O	=5.55062+01		

AQUEOUS SOLUTION EQUILIBRIA

COMPONENT	MOLALITY	ACTIVITY	ACTIVITY COEFFICIENT
H2O			9.995-01
H+	1.155-03	1.024-03	8.863-01
OH-	1.522-11	1.324-11	8.703-01
HSO3-	1.098-02	9.569-03	8.715-01
SO3--	9.464-07	5.460-07	5.769-01
SO4--	1.808-03	1.009-03	5.580-01
HCO3-	1.534-07	1.337-07	8.715-01
CO3--	1.143-14	6.594-15	5.769-01
NO3-	2.786-04	2.382-04	8.550-01
HSO4-	1.282-04	1.116-04	8.703-01
H2SO3	8.194-04	8.222-04	1.003+00
H2CO3	2.929-04	2.939-04	1.003+00
CA++	1.270-03	7.395-04	5.823-01
CAOH+	2.738-13	2.383-13	8.703-01
CASO3	1.058-06	1.062-06	1.003+00
CACO3	8.088-15	8.116-15	1.003+00
CAHCO3+	2.128-09	1.852-09	8.703-01
CASO4	1.587-04	1.593-04	1.003+00
CANO3+	4.724-07	4.112-07	8.703-01
MG++	3.593-04	2.061-04	5.737-01
MGOH+	1.270-12	1.105-12	8.703-01
MGSO3	9.761-08	9.795-08	1.003+00
MGHCO3+	2.946-10	2.564-10	8.703-01
MGSO4	4.066-05	4.080-05	1.003+00
MGCO3	3.561-15	3.573-15	1.003+00
NA+	1.176-02	1.030-02	8.758-01
NAOH	3.658-14	3.670-14	1.003+00
NACO3-	1.489-15	1.296-15	8.703-01
NAHCO3	7.714-10	7.740-10	1.003+00
NASO4-	6.427-05	5.594-05	8.703-01

NANO3		9.730-07	9.763-07	1.003+00
CL-		1.100-03	9.562-04	8.692-01

TYPE I, NO. 10A

PSO2 =7.75376-04 ATM.
PCO2 =9.50673-03 ATM.

MOLECULAR WATER = 9.99879-01 KGS.

PH = 2.990 IONIC STRENGTH = 1.96086-02 RES. E.N. = 1.251-09